

# Coordination Compounds

## 5.1 | DOUBLE SALTS AND COORDINATION COMPOUNDS

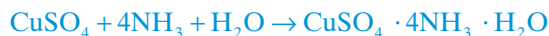
Addition compounds are formed when stoichiometric amounts of two or more stable compounds join together. For example:



carnallite



potassium alum



tetrammine copper(II)  
sulphate monohydrate



potassium ferrocyanide

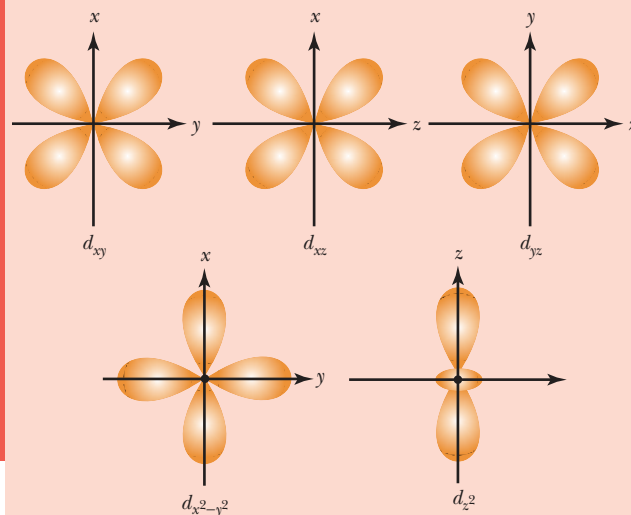
Addition compounds are of two types:

1. Those which lose their identity in solution (double salts)
2. Those which retain their identity in solution (complexes)

When crystals of carnallite are dissolved in water, the solution shows the properties of  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  ions. In a similar way, a solution of potassium alum shows the properties of  $\text{K}^+$ ,  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  ions. These are both examples of double salts which exist only in the crystalline state.

When the other two examples of coordination compounds dissolve they do not form simple ions –  $\text{Cu}^{2+}$ , or  $\text{Fe}^{2+}$  and  $\text{CN}^-$  – but instead their complex ions remain intact. Thus the cuproammonium ion  $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$  and the

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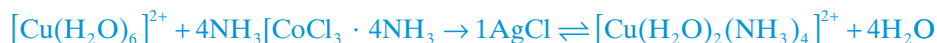


Shapes of *d* orbitals.

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ferrocyanide ion  $[\text{Fe}(\text{CN})_6]^{4-}$  exist as distinct entities both in the solid and in solution. Complex ions are shown by the use of square brackets. Compounds containing these ions are called coordination compounds. *The chemistry of metal ions in solution is essentially the chemistry of their complexes. Transition metal ions, in particular, form many stable complexes.* In solution ‘free’ metal ions are coordinated either to water or to other ligands. Thus  $\text{Cu}^{2+}$  exists as the pale blue complex ion  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  in aqueous solution (and also in hydrated crystalline salts). If aqueous ammonia is added to this solution, the familiar deep blue cuproammonium ion is formed:



Note that this reaction is a substitution reaction, and the  $\text{NH}_3$  replaces water in the complex ion.

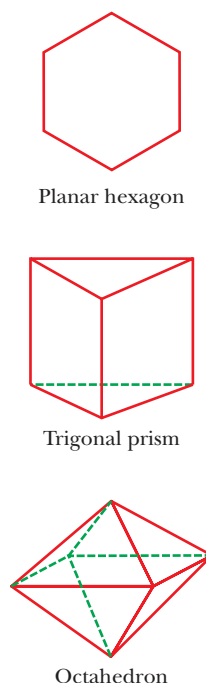
## 5.2 | WERNER'S WORK

Werner's coordination theory in 1893 was the first attempt to explain the bonding in coordination complexes. It must be remembered that this imaginative theory was put forward before the electron had been discovered by J.J. Thompson in 1896, and before the electronic theory of valency. This theory and his painstaking work over the next 20 years won Alfred Werner the Nobel Prize for Chemistry in 1913.

Complexes must have been a complete mystery without any knowledge of bonding or structure. For example, why does a stable salt like  $\text{CoCl}_3$  react with a varying number of stable molecules of a compound such as  $\text{NH}_3$  to give several new compounds:  $\text{CoCl}_3 \cdot 6\text{NH}_3$ ,  $\text{CoCl}_3 \cdot 5\text{NH}_3$  and  $\text{CoCl}_3 \cdot 4\text{NH}_3$ ? What are their structures? At that time X-ray diffraction, which is the most powerful method of determining the structures of crystals, had yet to be discovered. Werner did not have at his disposal any of the modern instrumental techniques, and all his studies were made using simple reaction chemistry. *Werner was able to explain the nature of bonding in complexes, and he concluded that in complexes the metal shows two different sorts of valency:*

- 1. Primary valencies:** These give rise to first order compounds (e.g.  $\text{CoCl}_3$  from cobalt and chlorine) and correspond to the valency (now known as oxidation state) of the central atom. These are non-directional. In modern terms, the number of primary valencies corresponds to the number of charges on the central metal atom. The complex  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  actually exists as  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $3\text{Cl}^-$ . Thus the primary valency is three. Similarly, in case of  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ , the primary valency is also three.
- 2. Secondary valencies:** These give rise to the higher order compounds (e.g.  $\text{CoCl}_3 \cdot n\text{NH}_3$  from  $\text{CoCl}_3$  and  $\text{NH}_3$ ). These are directional. In modern terms the number of secondary valencies equals the number of ligand atoms coordinated to the metal. This is now called the coordination number. Ligands are commonly negative ions such as  $\text{Cl}^-$ , or neutral molecules such as  $\text{NH}_3$ . Less commonly, ligands may be positive ions such as  $\text{NO}^+$ . Each metal has a characteristic number of secondary valencies. Thus in  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  the three  $\text{Cl}^-$  are held by primary valencies. The six  $\text{NH}_3$  groups are held by secondary valencies.

Werner also attempted to find the shapes of the complexes. The possible arrangements of six groups round one atom are a planar hexagon, a trigonal prism, and an octahedron (Figure 5.1). Werner then compared the number of isomeric forms he had obtained with the theoretical number for each of the possible shapes (Table 5.1).



**Figure 5.1** Possible geometric shapes for six-coordination.

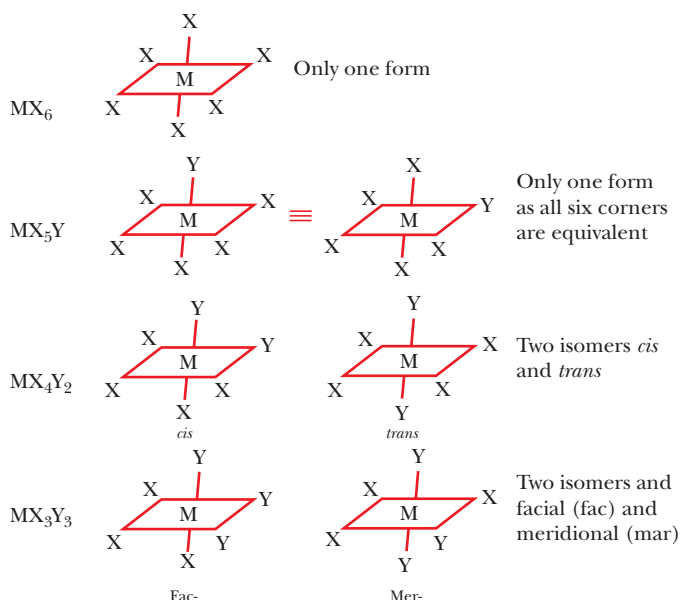
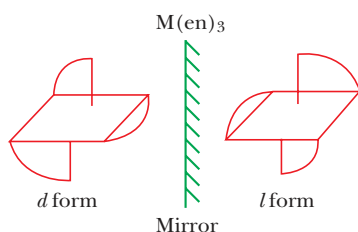
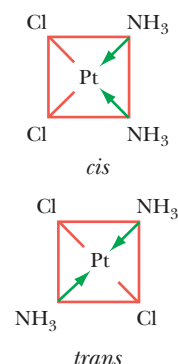
**Table 5.1** Number of isomers predicted and actually found

Complex	Observed	Predicted		
		Octahedral	Planar hexagon	Trigonal prism
$[MX_6]$	1	1	1	1
$[MX_5Y]$	1	1	1	1
$[MX_4Y_2]$	2	2	3	3
$[MX_3Y_3]$	2	2	3	3

These results strongly suggested that these complexes have an octahedral shape. This proof was not absolute proof, as it was just possible that the correct experimental conditions had not been found for preparing all the isomers. More recently the X-ray structures have been determined, and these establish that the shape is octahedral (Figure 5.2).

More recently, with a bidentate ligand such as ethylenediamine (1,2-diaminoethane), two optically active isomers of octahedral complexes have been found (Figure 5.3).

In a similar way, Werner studied a range of complexes which included  $[Pt^{II}(NH_3)_2Cl_2]$  and  $[Pd^{II}(NH_3)_2Cl_2]$ . The coordination number is 4, and the shape could be either tetrahedral or square planar. Werner was able to prepare two different isomers for these complexes. A tetrahedral complex can only exist in one form, but a square planar complex can exist in two isomeric forms. This proved these complexes are square planar rather than tetrahedral (Figure 5.4).

**Figure 5.2** Isomers in octahedral complexes.**Figure 5.3** Optical isomerism in octahedral complexes.**Figure 5.4** Isomerism in square planar complexes.

## 5.3 | MORE RECENT METHODS OF STUDYING COMPLEXES

The electrical conductivity of a solution of an ionic material depends on:

1. The concentration of solute.
2. The number of charges on the species which are formed on dissolution.

Molar conductivities relate to a 1 M solution and thus the concentration factor is removed. The total number of charges on the species formed when the complex dissolves can be deduced by comparison of its molar

conductivity with that of known simple ionic materials (Table 5.2). These conductivities suggest the same structures for the cobalt/ammonia/chlorine complexes mentioned earlier, as do the results from Werner's AgCl experiments, shown in Table 5.3.

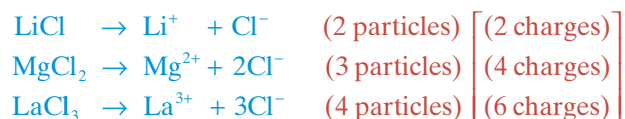
**Table 5.2** Conductivities of salts and complexes (molar conductivities measured at 0.001 M concentration)

	ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
LiCl → Li <sup>+</sup> + Cl <sup>-</sup> (total of 2 charges)	112.0
CaCl <sub>2</sub> → Ca <sup>2+</sup> + 2Cl <sup>-</sup> (total of 4 charges)	260.8
CoCl <sub>3</sub> · 5NH <sub>3</sub>	261.3
CoBr <sub>3</sub> · 5NH <sub>3</sub>	257.6
LaCl <sub>3</sub> → La <sup>3+</sup> + 3Cl <sup>-</sup> (total of 6 charges)	393.5
CoCl <sub>3</sub> · 6NH <sub>3</sub>	431.6
CoBr <sub>3</sub> · 6NH <sub>3</sub>	426.9

**Table 5.3** Number of charges related to modern and Werner structures

	Charges	Primary valency	Ionizable chlorines	Secondary valency
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> 3Cl <sup>-</sup>	6	3	3	6NH <sub>3</sub> = 6
[Co(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>2+</sup> 2Cl <sup>-</sup>	4	3	2	5NH <sub>3</sub> + 1 Cl <sup>-</sup> = 6
[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup> Cl <sup>-</sup>	2	3	1	4NH <sub>3</sub> + 2Cl <sup>-</sup> = 6

The freezing point of a liquid is lowered when a chemical substance is dissolved in it. Cryoscopic measurements involve measuring how much the freezing point is lowered. The depression of freezing point obtained depends on the number of particles present. Cryoscopic measurements can be used to find if a molecule dissociates, and how many ions are formed. If a molecule dissociates into two ions it will give twice the expected depression for a single particle. If three ions are formed this will give three times the expected depression. Thus:



The number of particles formed from a complex molecule determines the size of the depression of freezing point. Note that the number of particles formed may be different from the total number of charges which can be obtained from conductivity measurements. These two types of information can be used together to establish the structure (Table 5.4).

**Table 5.4** Establishing the structure of complexes

Formula	Cryoscopic measurement	Molar conductivity	Structure
CoCl <sub>3</sub> · 6NH <sub>3</sub>	4 particles	6 charges	[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> 3Cl <sup>-</sup>
CoCl <sub>3</sub> · 5NH <sub>3</sub>	3 particles	4 charges	[Co(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>2+</sup> 2Cl <sup>-</sup>
CoCl <sub>3</sub> · 4NH <sub>3</sub>	2 particles	2 charges	[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup> Cl <sup>-</sup>
CoCl <sub>3</sub> · 3NH <sub>3</sub>	1 particle	0 charge	[Co(NH <sub>3</sub> ) <sub>3</sub> Cl <sub>3</sub> ]
Co(NO <sub>2</sub> ) <sub>3</sub> · KNO <sub>2</sub> · 2NH <sub>3</sub>	2 particles	2 charges	K <sup>+</sup> [Co(NH <sub>3</sub> ) <sub>2</sub> (NO <sub>2</sub> ) <sub>4</sub> ] <sup>-</sup>
Co(NO <sub>2</sub> ) <sub>3</sub> · 2KNO <sub>2</sub> · NH <sub>3</sub>	3 particles	4 charges	2K <sup>+</sup> [Co(NH <sub>3</sub> )(NO <sub>2</sub> ) <sub>5</sub> ] <sup>2-</sup>
Co(NO <sub>2</sub> ) <sub>3</sub> · 3KNO <sub>2</sub>	4 particles	6 charges	3K <sup>+</sup> [Co(NO <sub>2</sub> ) <sub>6</sub> ] <sup>3-</sup>

The magnetic moment can be measured and this provides information about the number of unpaired electron spins present in a complex. From this it is possible to decide how the electrons are arranged and which orbitals are occupied. Sometimes the structure of the complex can be deduced from this. For example, the compound  $\text{Ni}^{\text{II}}(\text{NH}_3)_4(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  might contain four ammonia molecules coordinated to Ni in a square planar  $[\text{Ni}(\text{NH}_3)_4]^{2+}$  ion and two molecules of water of crystallization and have no unpaired electrons. Alternatively the water might be coordinated to the metal, giving an octahedral  $[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$  complex with two unpaired electrons. Both these complex ions exist and their structures can be deduced from magnetic measurements.

Dipole moments may also yield structural information but only for non-ionic complexes. For example, the complex  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  is square planar, and can exist as *cis* or *trans* forms. The dipole moments from the various metal–ligand bonds cancel out in the *trans* configuration. However, a finite dipole moment is given by the *cis* arrangement (Figure 5.4).

Electronic spectra (UV and visible) also provide valuable information on the energy of the orbitals, and on the shape of the complex. By this means it is possible to distinguish between tetrahedral and octahedral complexes, and whether the shape is distorted or regular.

The most powerful method, however, is the X-ray determination of the crystal structure. This provides details of the exact shape and the bond lengths and angles of the atoms in the structure.

## 5.4 | CLASSIFICATION OF LIGANDS

There are several ways to classify ligands and these are discussed as follows:

### 1. Based upon charges

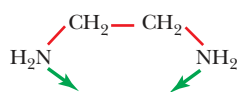
- Neutral ligands:  $\text{H}_2\text{O}$ ,  $\text{NO}$ ,  $\text{CO}$ ,  $\text{C}_6\text{H}_6$ , etc.
- Positive ligands:  $\text{NO}^+$  and  $\text{NH}_2^+ - \text{NH}_3$
- Negative ligands:  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{CN}^-$ ,  $\text{OH}^-$

### 2. Based upon denticity of the ligand

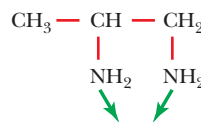
The number of donations accepted by a central atom from a particular ligand is known as the denticity of the ligand. Ligands may be classified as follows based on their denticity:

- Monodentate:** Only one donation is accepted from the ligand. For example,  $\text{H}_2\text{O}$ ,  $\text{NO}$ ,  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ , etc.
- Bidentate:** Two donations are accepted from the ligand. For example,

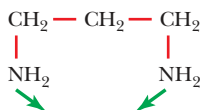
(i) en: ethylenediamine



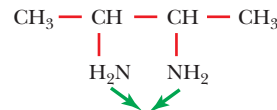
(ii) pn: propylenediamine



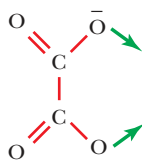
(iii) tn: trimethylenediamine



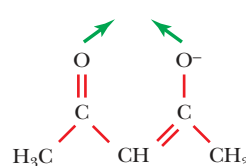
(iv) bn: butylenediamine

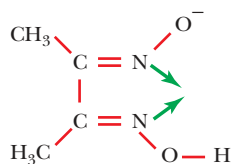
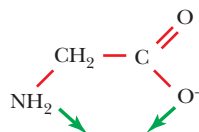


(v)  $\text{ox}^{2-}$ : oxalate

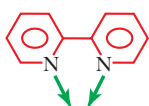
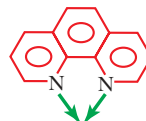
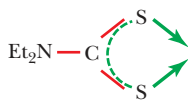


(vi)  $\text{acac}^-$ : acetylacetonate

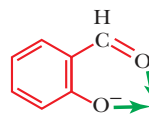


(vii)  $\text{dmg}^-$ : dimethylglyoximate(viii)  $\text{gly}^-$ : glycinate

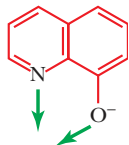
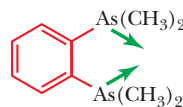
(ix) dipy: dipyridyl

(x) *o*-phen: *ortho*-phenanthroline(xi)  $\text{N,N'}$ -Diethylthiocarbamate ion

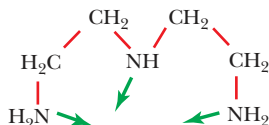
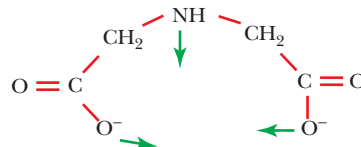
(xii) Salicylaldehyde anion



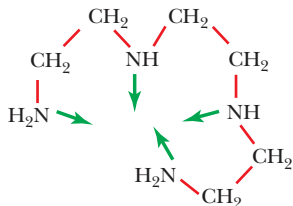
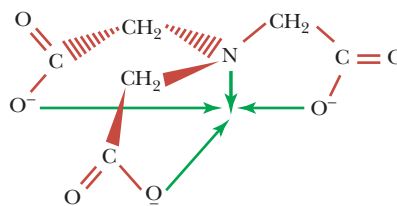
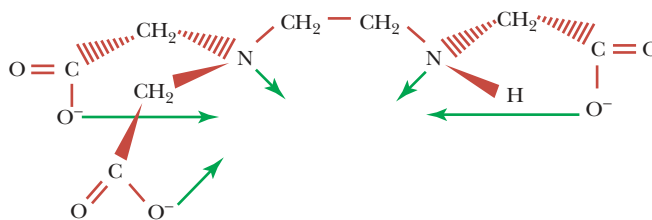
(xiii) 8-Hydroxyquinolinol ion (oxine)

(xiv) *o*-Phenylenebisdimethylarsine (diarsine)**c. Tridentate:** Three donations are accepted from the ligand. For example,

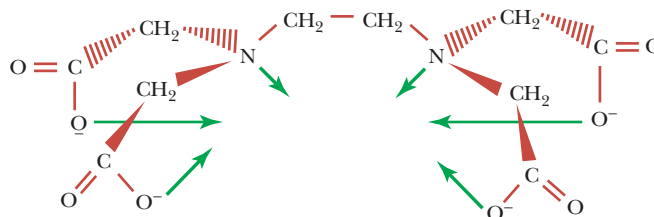
(i) dien: diethylenetriamine

(ii)  $\text{imda}^{2-}$ : iminodiacetate**d. Tetradentate:** Four donations are accepted from the ligand. For example,

(i) trien: triethylenetetraamine

(ii)  $\text{NTA}^{3-}$ : nitrilotriacetate**e. Pentadentate:** Five donations are accepted from the ligand. For example, $\text{EDTA}^{3-}$ : ethylenediamine triacetate

- f. Hexadentate:** Six donations are accepted from the ligand. For example, EDTA<sup>4-</sup>: ethylenediamine tetracetate

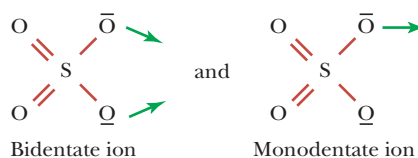


**Note:**

- 1. Flexidentate:** A ligand which shows variable denticity is called a flexidentate ligand.

For example,

(i)



- (ii)  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Br}$  (iii)  $\text{NO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{S}_2\text{O}_3^{2-}$   
 $\text{CO}_3^{2-}$  is bidentate  $\text{CO}_3^{2-}$  is monodentate may also act as flexidentate ligand

- 2. Chelating:** A ligand that can form a ring structure with the central atom is called a chelating ligand.

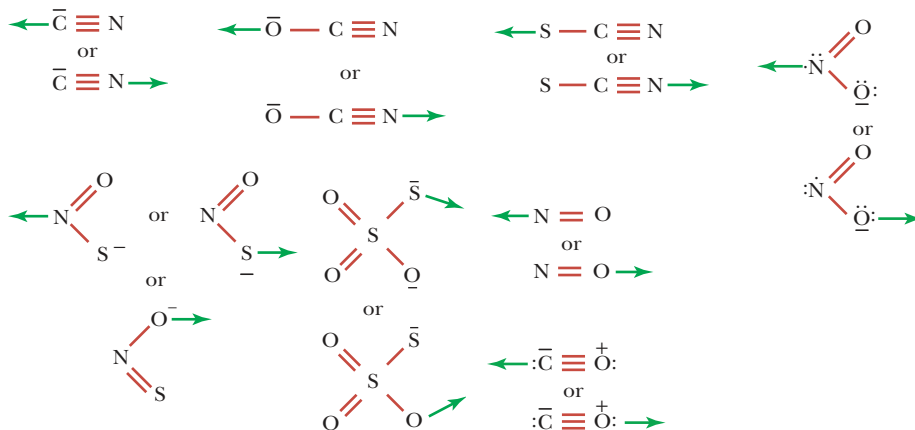
All polydentate ligands are the example of chelating ligands.

Chelated complexes are more stable than similar complexes with monodentate ligands as dissociation of the complex involves breaking two bonds rather than one.

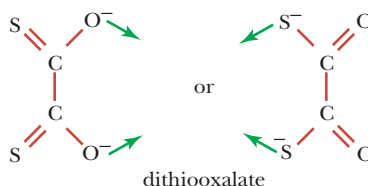
However, it must be noted that  $\text{NH}_2\text{NH}_2$  and  $\text{N}(\text{CH}_2 - \text{CH}_2)_3\text{N}$  cannot act as chelating ligands due to the formation of three membered ring and locked structure, respectively.

- 3. Ambidentate ligand:** A ligand that may have more than one kind of donor sites but at a time only one kind of donor site is utilized for donation is called as ambidentate ligand. Ambidentate ligand may be of two types.

**a. Monodentate and ambidentate:**



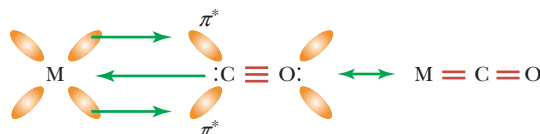
**b. Bidentate and ambidentate:**



### 3. Based upon bonding interaction between the ligand and the central atom

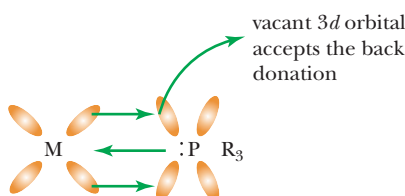
- a. Classical or simple donor ligand:** These ligands only donate the lone pair of electrons to the central atom. For example,  $\text{O}^{2-}$ ,  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{NH}_2^-$ ,  $\text{NH}_3$ ,  $\text{N}^{3-}$ , etc.
- b. Non-classical or  $\pi$ -acid or  $\pi$ -acceptor ligand:** These ligands not only donate the lone pair of electrons to the central atom but also accept the electron cloud from the central atom in their low-lying vacant orbitals. This kind of back donation is known as 'synergic effect' or 'synergic bonding'. For example,  $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{NO}^+$ ,  $\text{PF}_3$ ,  $\text{PR}_3$  ( $\text{R} = \text{H}, \text{Et}, \text{Ph} \dots$ ),  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{CO}_2$ , etc.

(i) In case of  $\text{CO}$ , the back donation to the  $\pi^*$  orbital of central atom may be depicted as:

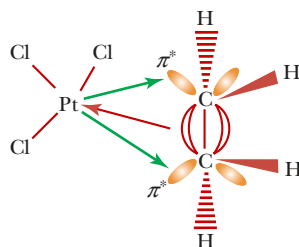


By valence bond or molecular orbital theory, it is well understood that the bond order of  $\text{C}-\text{O}$  bond decreases but the  $\text{C}-\text{O}$  bond length must increase due to synergic effect. Similarly, as  $\text{CN}^-$  and  $\text{NO}^+$  are isoelectronic with  $\text{CO}$ , so back donation takes place in these species also in the  $\pi^*$  orbitals and the same conclusion can be drawn for the bond order and bond lengths.

(ii) In case of  $\text{PR}_3$ , the back donation may be depicted as:



(iii) In case of  $\text{C}_2\text{H}_4$ , the back donation may be depicted using the example of Zeise's salt.



Here the back donation is accepted in the  $\pi^*$  orbital of  $\text{C}-\text{C}$  bond. Hence, the bond order of  $\text{C}-\text{C}$  bond decreases and the bond length increases as compared to free  $\text{C}_2\text{H}_4$  molecule. Due to backbonding,  $\text{C}_2\text{H}_4$  molecule loses its planarity. Similarly,  $\text{C}_2\text{H}_2$  molecule loses its linearity not the planarity.

## 5.5 | EFFECTIVE ATOMIC NUMBER (EAN)

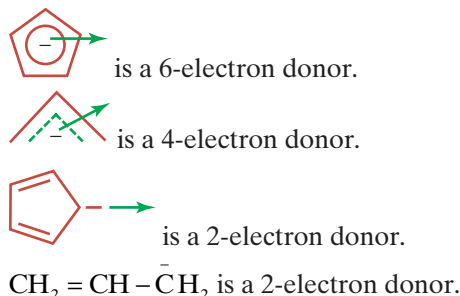
Physically EAN signifies the number of electrons available around a central atom within a complex, including the electrons accepted from ligands. It is mathematically defined as follows:

$$\begin{aligned} \text{EAN of a central atom in a complex} &= \text{Atomic number of the central atom (Z)} \\ &\quad - (\text{oxidation number of the central atom with sign}) \\ &\quad + (\text{number of electrons collected from the ligands}). \end{aligned}$$



The following points need to be noted with regard to EAN.

1. All donations contribute two electrons, while NO is considered as a 3-electron donor.
2. For  $\pi$ -donors, the number of  $\pi$ -electrons involved in donation from a particular ligand are to be considered. For example,



3. For the compounds having  $\delta$ -bond, for example,  $\text{Mn}_2(\text{Co})_{10}$ , the EAN of each Mn atom is calculated as:

$$\text{EAN of Mn} = \frac{1}{2}[2 \times 25 - 0 + 10 \times 2 + 2^*] = 36$$

\*These two electrons are considered for  $\delta$ -bond.

The EAN of some metal atoms in different complexes are given in Table 5.5.

**Table 5.5** Effective atomic numbers of some metals in complexes

Atom	Atomic number	Complex	Electrons lost in ion formation	Electrons gained by coordination	EAN
Cr	24	$[\text{Cr}(\text{CO})_6]$	0	12	36
Fe	26	$[\text{Fe}(\text{CN})_6]^{4-}$	2	12	36
Fe	26	$[\text{Fe}(\text{CO})_5]$	0	10	36
Co	27	$[\text{Co}(\text{NH}_3)_6]^{3+}$	3	12	36
Ni	28	$[\text{Ni}(\text{CO})_4]$	0	8	36
Cu	29	$[\text{Cu}(\text{CN})_4]^{3-}$	1	8	36
Pd	46	$[\text{Pd}(\text{NH}_3)_6]^{4+}$	4	12	54 (Xe)
Pt	78	$[\text{PtCl}_6]^{2-}$	4	12	86 (Rn)
Fe	26	$[\text{Fe}(\text{CN})_6]^{3-}$	3	12	35
Ni	28	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	2	12	38
Pd	46	$[\text{PdCl}_4]^{2-}$	2	8	52
Pt	78	$[\text{Pt}(\text{NH}_3)_4]^{2+}$	2	8	84
Ti	22	$[\text{Ti}(\sigma\text{-C}_5\text{H}_5)_2(\pi\text{-C}_5\text{H}_5)_2]^0$	4	16	34
Fe	26	$[\text{Fe}(\pi\text{-C}_5\text{H}_5)_2]^0$	2	12	36
Fe	26	$[\text{Fe}(\text{CO})_2(\text{NO})_2]^0$	0	10	36
Co	27	$[\text{Co}(\text{CO})_4]^-$	-1	8	36
V	23	$[\text{V}(\text{CO})_6]^-$	-1	12	36

### Sidgwick EAN rule

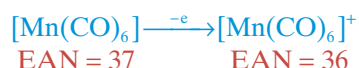
In 1927, Sidgwick suggested that electron pairs from ligands were added to the central metal atom until the central atom was surrounded by the same number of electrons as the next noble gas. The stability of the resulting state can be explained on the basis of the molecular orbital theory. However, this rule fails in many cases and works best for metals in low oxidation state.

Metal carbonyls exhibit a strong tendency to achieve Sidgwick EAN values and as a result of this:

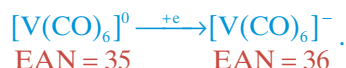
1. The number of CO molecule attached in mononuclear carbonyls can be predicted. For example, in



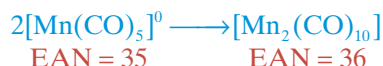
2.  $[\text{Mn}(\text{CO})_6]^0$  can act as a reducing agent. The complex loses an electron to attain the noble gas configuration and hence obey Sidgwick EAN rule.



3.  $[\text{V}(\text{CO})_6]^0$  can act as oxidizing agent. The complex gains an electron to attain the noble gas configuration and hence obey Sidgwick EAN rule.



4.  $[\text{Mn}(\text{CO})_5]^0$  undergoes dimerization to attain the noble gas configuration and hence obey Sidgwick EAN rule.



## 5.6 | SHAPES OF $d$ ORBITALS

Since  $d$  orbitals are often used in coordination complexes it is important to study their shapes and distribution in space. The five  $d$  orbitals are not identical and the orbitals may be divided into two sets. The three  $t_{2g}$  orbitals have identical shape and point between the axes,  $x$ ,  $y$  and  $z$ . The two  $e_g$  orbitals have different shapes and point along the axes (Figure 5.5). Alternative names for  $t_{2g}$  and  $e_g$  are  $d_{xy}$  and  $d_{yz}$  respectively.

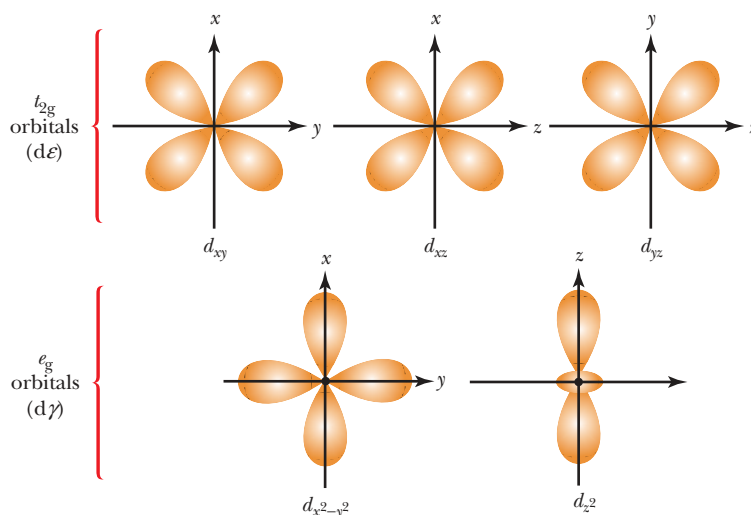


Figure 5.5 Shapes of  $d$  orbitals.

## 5.7 | BONDING IN TRANSITION METAL COMPLEXES

There are three theories of metal to ligand bonding in complexes, all dating back to the 1930s.

### Valence bond theory

This theory was developed by Pauling. Coordination compounds contain complex ions, in which ligands form coordinate bonds to the metal. Thus the ligand must have a lone pair of electrons, and the metal must have an empty orbital of suitable energy available for bonding. The theory considers which atomic orbitals on the metal are used for bonding. From this the shape and stability of the complex are predicted. The theory has two main limitations. Most transition metal complexes are coloured, but the theory provides no explanation for their electronic spectra. Further, the theory does not explain why the magnetic properties vary with temperature. For these reasons it has largely been superseded by the crystal field theory. However, it is of interest for study as it shows the continuity of the development of modern ideas from Werner's theory.

### Crystal field theory

This theory was proposed by Bethe and van Vleck. The attraction between the central metal and ligands in the complex is considered to be purely electrostatic. Thus bonding in the complex may be ion-ion attraction (between positive and negative ions such as  $\text{Co}^{3+}$  and  $\text{Cl}^-$ ). Alternatively, ion-dipole attractions may give rise to bonding (if the ligand is a neutral molecule such as  $\text{NH}_3$  or  $\text{CO}$ ).  $\text{NH}_3$  has a dipole moment with a  $\delta^-$  charge on N and  $\delta^+$  charges on H. Thus in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  the  $\delta^-$  charge on the N atom of each  $\text{NH}_3$  points towards the  $\text{Co}^{3+}$ . This theory is simple. It has been remarkably successful in explaining the electronic spectra and magnetism of transition metal complexes, particularly when allowance is made for the possibility of some covalent interaction between the orbitals on the metal and ligand. When some allowance is made for covalency, the theory is often renamed as the ligand field theory. Three types of interaction are possible:  $\sigma$  overlap of orbitals,  $\pi$  overlap of orbitals, or  $d\pi-p\pi$  bonding (back bonding) due to  $\pi$  overlap of full  $d$  orbitals on the metal with empty  $p$  orbitals on the ligands.

### Molecular orbital theory

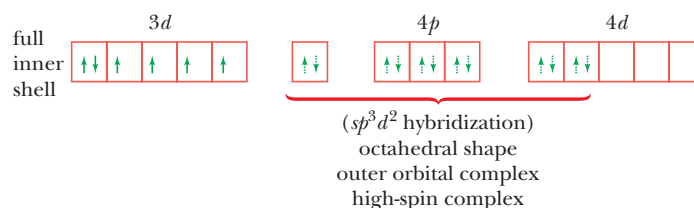
Both covalent and ionic contributions are fully allowed for in this theory. Though this theory is probably the most important approach to chemical bonding, it has not displaced the other theories. This is because the quantitative calculations involved are difficult and lengthy, involving the use of extensive computer time. Much of the qualitative description can be obtained by other approaches using symmetry and group theory.

## 5.8 | VALENCE BOND THEORY

The formation of a complex may be considered as a series of hypothetical steps. First the appropriate metal ion is taken, e.g.  $\text{Co}^{3+}$ . A Co atom has the outer electronic structure  $3d^7 4s^2$ . Thus a  $\text{Co}^{3+}$  ion will have the structure  $3d^6$ , and the electrons will be arranged:



If this ion forms a complex with six ligands, then six empty atomic orbitals are required on the metal ion to receive the coordinated lone pairs of electrons. The orbitals used are the  $4s$ , three  $4p$  and two  $4d$ . These are hybridized to give a set of six equivalent  $sp^3d^2$  hybrid orbitals. A ligand orbital containing a lone pair of electrons forms a coordinate bond by overlapping with an empty hybrid orbital on the metal ion. In this way a  $\sigma$  bond is formed with each ligand. The  $d$  orbitals used are the  $4d_{x^2-y^2}$  and  $4d_{z^2}$ . In the diagrams below, electron pairs from the ligands are shown as  $\uparrow\downarrow$ .

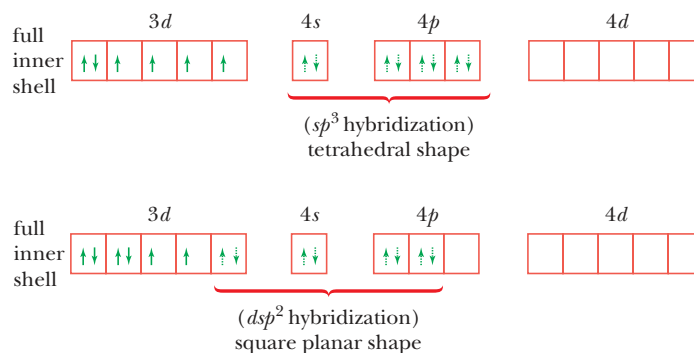


Since the outer 4d orbitals are used for bonding this is called an *outer orbital complex*. The energy of these orbitals is quite high, so that the complex will be reactive or labile. The magnetic moment depends on the number of unpaired electrons. The 3d level contains the maximum number of unpaired electrons for a  $d^6$  arrangement, so this is sometimes called a *high-spin* or a *spin-free complex*. An alternative octahedral arrangement is possible when the electrons on the metal ion are rearranged as shown below. As before, lone pairs from the ligands are shown as  $\uparrow\downarrow$ .



Since low energy inner d orbitals are used this is called an *inner orbital complex*. Such complexes are more stable than the outer orbital complexes. The unpaired electrons in the metal ion have been forced to pair up, and so this is now a low-spin complex. In this particular case all the electrons are paired, so the complex will be diamagnetic.

The metal ion could also form four-coordinate complexes, and two different arrangements are possible. *It must be remembered that hybrid orbitals do not actually exist.* Hybridization is a mathematical manipulation of the wave equations for the atomic orbitals involved.



The theory does not explain the colour and spectra of complexes. The theory shows the number of unpaired electrons and from this the magnetic moment can be calculated. However, it does not explain why the magnetic moment varies with temperature.

## 5.9 | CRYSTAL FIELD THEORY

The crystal field theory is now much more widely accepted than the valence bond theory. It assumes that the attraction between the central metal and the ligands in a complex is purely electrostatic. The transition metal which forms the central atom in the complex is regarded as a positive ion of charge equal to the oxidation state. This is surrounded by negative ligands or neutral molecules which have a lone pair of electrons. If the ligand is a neutral molecule such as  $\text{NH}_3$ , the negative end of the dipole in the molecule is directed towards the metal ion. The electrons on the central metal are under repulsive forces from those

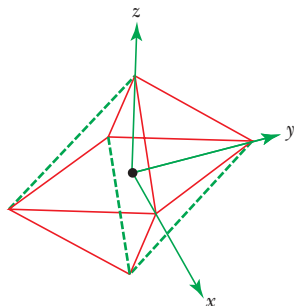
on the ligands. Thus the electrons occupy the  $d$  orbitals furthest away from the direction of approach of ligands. In the crystal field theory the following assumptions are made.

1. Ligands are treated as point charges.
2. There is no interaction between metal orbitals and ligand orbitals.
3. The  $d$  orbitals on the metal all have the same energy (that is degenerate) in the free atom. However, when a complex is formed the ligands destroy the degeneracy of these orbitals, i.e. the orbitals now have different energies. In an isolated gaseous metal ion, the five  $d$  orbitals do all have the same energy, and are termed degenerate. If a spherically symmetrical field of negative charges surrounds the metal ion, the  $d$  orbitals remain degenerate. However, the energy of the orbitals is raised because of repulsion between the field and the electrons on the metal. In most transition metal complexes, either six or four ligands surround the metal, giving octahedral or tetrahedral structures. In both of these cases the field produced by the ligands is not spherically symmetrical. Thus the  $d$  orbitals are not all affected equally by the ligand field.

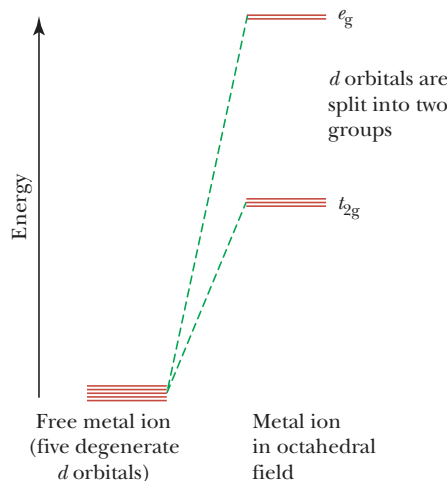
### Octahedral complexes

In an octahedral complex, the metal is at the centre of the octahedron, and the ligands are at the six corners. The directions  $x$ ,  $y$  and  $z$  point to three adjacent corners of the octahedron as shown in Figure 5.6.

The lobes of the  $e_g$  orbitals ( $d_{x^2-y^2}$  and  $d_{z^2}$ ) point along the axes  $x$ ,  $y$  and  $z$ . The lobes of the  $t_{2g}$  orbitals ( $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ ) point in between the axes. It follows that the approach of six ligands along the  $x$ ,  $y$ ,  $z$ ,  $-x$ ,  $-y$  and  $-z$  directions will increase the energy of the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals (which point along the axes) much more than it increases the energy of the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals (which point between the axes). Thus under the influence of an octahedral ligand field the  $d$  orbitals split into two groups of different energies (Figure 5.7).



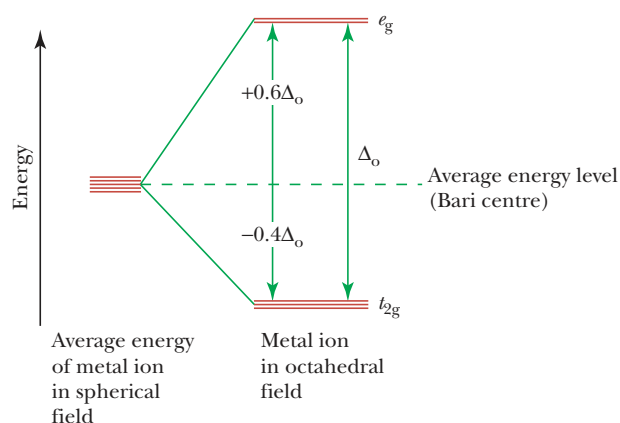
**Figure 5.6** The directions in an octahedral complex.



**Figure 5.7** Crystal field splitting of energy levels in an octahedral field.

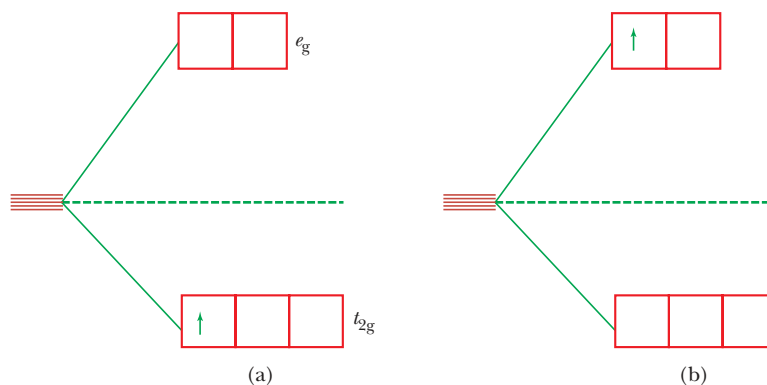
Rather than referring to the energy level of an isolated metal atom, the weighted mean of these two sets of perturbed orbitals is taken as the zero: this is sometimes called the Bari centre. The difference in energy between the two  $d$  levels is given either of the symbols  $\Delta_o$  or  $10 Dq$ . It follows that the  $e_g$  orbitals are  $+0.6\Delta_o$  above the average level, and the  $t_{2g}$  orbitals are  $-0.4\Delta_o$  below the average (Figure 5.8).

The size of the energy gap  $\Delta_o$  between the  $t_{2g}$  and  $e_g$  levels can be measured easily by recording the UV-visible spectrum of the complex. Consider a complex like  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ . The  $\text{Ti}^{3+}$  ion has one  $d$  electron.



**Figure 5.8** Diagram of the energy levels of  $d$  orbitals in an octahedral field.

In the complex this will occupy the orbital with the lowest energy, that is one of the  $t_{2g}$  orbitals (Figure 5.9a). The complex absorbs light of the correct wavelength (energy) to promote the electron from the  $t_{2g}$  level to the  $e_g$  level (Figure 5.9b).



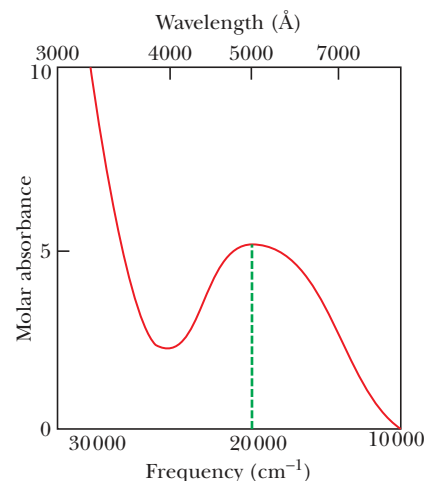
**Figure 5.9**  $d^1$  configuration: (a) ground state, (b) excited state.

The electronic spectrum for  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is given in Figure 5.10. The steep part of the curve from 27 000 to 30 000  $\text{cm}^{-1}$  (in the UV region) is due to charge transfer. The  $d-d$  transition is the single broad peak with a maximum at 20 300  $\text{cm}^{-1}$ . Since  $1 \text{ kJ mol}^{-1} = 83.7 \text{ cm}^{-1}$ , the value of  $\Delta_o$  for  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is  $20\,300/83.7 = 243 \text{ kJ mol}^{-1}$ . This is much the same as the energy of many normal single bonds (see Appendix F).

The above method is the most convenient way of measuring  $\Delta_o$  values. However,  $\Delta_o$  values can also be obtained from values of observed lattice energies and those calculated using the Born-Landé equation (see Chapter 3).

Solutions containing the hydrated  $\text{Ti}^{3+}$  ion are reddish violet coloured. This is because yellow and green light are absorbed to excite the electron. Thus the transmitted light is the complementary colour red-violet (Table 5.6).

Because of the crystal field splitting of  $d$  orbitals, the single  $d$  electron in  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  occupies an energy level  $2/5\Delta_o$  below the average energy of the  $d$  orbitals. As a result the complex is more stable. The crystal field stabilization energy (CFSE) is in this case  $2/5 \times 243 = 97 \text{ kJ mol}^{-1}$ .



**Figure 5.10** Ultraviolet and visible absorption spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ .

**Table 5.6** Colours absorbed and colours observed

Colour absorbed	Colour observed	Wavenumber observed ( $\text{cm}^{-1}$ )
Yellow–green	Red–violet	24 000–26 000
Yellow	Indigo	23 000–24 000
Orange	Blue	21 000–23 000
Red	Blue–green	20 000–21 000
Purple	Green	18 000–20 000
Red–violet	Yellow–green	17 300–18 000
Indigo	Yellow	16 400–17 300
Blue	Orange	15 300–16 400
Blue–green	Red	12 800–15 300

The magnitude of  $\Delta_o$  depends on three factors:

1. The nature of the ligands.
2. The charge on the metal ion.
3. Whether the metal is in the first, second or third row of transitions elements.

Examination of the spectra of a series of complexes of the same metal with different ligands shows that the position of the absorption band (and hence the value of  $\Delta_o$ ) varies depending on the ligands which are attached (Table 5.7).

**Table 5.7** Crystal field splittings by various ligands

Complex	Absorption peak	
	( $\text{cm}^{-1}$ )	( $\text{kJ mol}^{-1}$ )
$[\text{Cr}^{\text{III}}\text{Cl}_6]^{3-}$	13 640	163
$[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$	17 830	213
$[\text{Cr}^{\text{III}}(\text{NH}_3)_6]^{3+}$	21 680	259
$[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$	26 280	314

Ligands which cause only a small degree of crystal field splitting are termed weak field ligands. Ligands which cause a large splitting are called strong field ligands. Most  $\Delta$  values are in the range  $7000 \text{ cm}^{-1}$  to  $30,000 \text{ cm}^{-1}$ . The common ligands can be arranged in ascending order of crystal field splitting  $\Delta$ . The order remains practically constant for different metals, and this series is called the spectrochemical series.

#### Spectrochemical series

*weak field ligands*

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{EtOH} < \text{oxalate} < \text{H}_2\text{O}$   
 $< \text{EDTA} < (\text{NH}_3 \text{ and pyridine}) < \text{ethylenediamine} < \text{dipyridyl}$   
 $< o\text{-phenanthroline} < \text{NO}_2^- < \text{CN}^- < \text{CO}$

*strong field ligands*

The spectrochemical series is an experimentally determined series. It is difficult to explain the order as it incorporates both the effects of  $\sigma$  and  $\pi$  bonding. The halides are in the order expected from electrostatic effects. In other cases we must consider covalent bonding to explain the order. A pattern of increasing  $\sigma$  donation is followed:

halide donors < O donors < N donors < C donors

The crystal field splitting produced by the strong field  $\text{CN}^-$  ligand is about double that for weak field ligands like the halide ions. This is attributed to  $\pi$  bonding in which the metal donates electrons from a filled  $t_{2g}$

orbital into a vacant orbital on the ligand. In a similar way, many unsaturated N donors and C donors may also act as  $\pi$  acceptors.

The magnitude of  $\Delta_o$  increases as the charge on the metal ion increases.

**Table 5.8** Crystal field splittings for hexa-aqua complexes of  $M^{2+}$  and  $M^{3+}$

Oxidation state		Ti	V	Cr	Mn	Fe	Co	Ni	Cu
(+II)	Electronic configuration	$d^2$	$d^3$	$d^4$	$d^5$	$d^6$	$d^7$	$d^8$	$d^9$
	$\Delta_o$ in $\text{cm}^{-1}$	–	12 600	13 900	7 800	10 400	9 300	8500	12 600
	$\Delta_o$ in $\text{kJ mol}^{-1}$	–	151	(166)	93	124	111	102	(151)
(+ III)	Electronic configuration	$d^1$	$d^2$	$d^3$	$d^4$	$d^5$	$d^6$	$d^7$	$d^8$
	$\Delta_o$ in $\text{cm}^{-1}$	20 300	18 900	17 830	21 000	13 700	18 600	–	–
	$\Delta_o$ in $\text{kJ mol}^{-1}$	243	226	213	(251)	164	222	–	–

Note: Values in paranthesis for  $d^4$  and  $d^9$  are approximate because of tetragonal distortion.

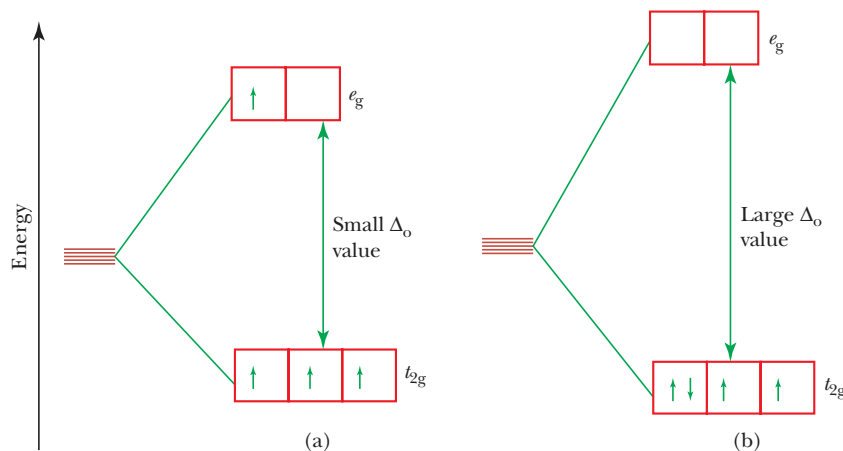
**Table 5.9**  $\Delta_o$  crystal field splittings in one group

	$\text{cm}^{-1}$	$\text{kJ mol}^{-1}$
$[\text{Co}(\text{NH}_3)_6]^{3+}$	24 800	296
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34 000	406
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41 000	490

For first row transition metal ions, the values of  $\Delta_o$  for  $M^{3+}$  complexes are roughly 50% larger than the values for  $M^{2+}$  complexes (Table 5.8).

The value of  $\Delta_o$  also increases by about 30% between adjacent members down a group of transition elements (Table 5.9). The crystal field stabilization energy in  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , which has a  $d^1$  configuration, has previously been shown to be  $-0.4\Delta_o$ . In a similar way, complexes containing a metal ion with a  $d^2$  configuration will have a CFSE of  $2 \times -0.4\Delta_o = -0.8\Delta_o$ , by singly filling two of the  $t_{2g}$  orbitals. (This is in agreement with Hund's rule that the arrangement with the maximum number of unpaired electrons is the most stable.) Complexes of  $d^3$  metal ions have a CFSE of  $3 \times -0.4\Delta_o = -1.2\Delta_o$ .

Complexes with a metal ion with a  $d^4$  configuration would be expected to have an electronic arrangement in accordance with Hund's rule (Figure 5.11a) with four unpaired electrons, and the CFSE will be  $(3 \times -0.4\Delta_o) + (0.6\Delta_o) = -0.6\Delta_o$ . An alternative arrangement of electrons which does not comply with Hund's rule is shown in Figure 5.11b. This arrangement has two unpaired electrons, and the CFSE is



**Figure 5.11** High- and low-spin complexes: (a)  $d^4$  high-spin arrangement (weak ligand field); (b)  $d^4$  low-spin arrangement (strong ligand field).



**Table 5.10** CFSE and pairing energy for some complexes

Complex	Configuration	$\Delta_o$ (cm <sup>-1</sup> )	$P$ (cm <sup>-1</sup> )	Predicted	Found
[Fe <sup>II</sup> (H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	$d^6$	10 400	17 600	high spin	High spin
[Fe <sup>II</sup> (CN) <sub>6</sub> ] <sup>4-</sup>	$d^6$	32 850	17 600	low spin	Low spin
[Co <sup>III</sup> F <sub>6</sub> ] <sup>3-</sup>	$d^6$	13 000	21 000	high spin	High spin
[Co <sup>III</sup> (NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	$d^6$	23 000	21 000	low spin	Low spin

$(4 \times -0.4\Delta_o) = -1.6\Delta_o$ . The CFSE is larger than in the previous case. However, the energy  $P$  used to pair the electrons must be allowed for, so the total stabilization energy is  $-1.6\Delta_o + P$ . These two arrangements differ in the number of unpaired electrons. The one with the most unpaired electrons is called ‘high-spin’ or ‘spin-free’, and the other one the ‘low-spin’ or ‘spin-paired’ arrangement. Both arrangements have been found to exist. Which arrangement occurs for any particular complex depends on whether the energy to promote an electron to the upper  $e_g$  level (that is the crystal field splitting  $\Delta_o$ ) is greater than the energy to pair electrons (that is  $P$ ) in the lower  $t_{2g}$  level. For a given metal ion  $P$  is constant. Thus the amount of crystal field splitting is determined by the strength of the ligand field. A weak field ligand such as  $\text{Cl}^-$  will only cause a small splitting of energy levels  $\Delta_o$ . Thus it will be more favourable energetically for electrons to occupy the upper  $e_g$  level and have a high-spin complex, rather than to pair electrons. In a similar way, strong field ligands such as  $\text{CN}^-$  cause a large splitting  $\Delta_o$ . In this case it requires less energy to pair the electrons and form a low-spin complex. (see Table 5.10.).

Similar arguments apply to high- and low-spin complexes of metal ions with  $d^5$ ,  $d^6$  and  $d^7$  configurations. These are summarized in Table 5.11.

**Table 5.11** CFSE and electronic arrangements in octahedral complexes

Number of $d$ electrons	Arrangement in weak ligand field				Arrangement in strong ligand field			
	$t_{2g}$	$e_g$	CFSE $\Delta_o$	Spin only magnetic moment $\mu_s(D)$	$t_{2g}$	$e_g$	CFSE $\Delta_o$	Spin only magnetic moment $\mu_s(D)$
$d^1$			-0.4	1.73			-0.4	1.73
$d^2$			-0.8	2.83			-0.8	2.83
$d^3$			-1.2	3.87			-1.2	3.87
$d^4$			-1.2 +0.6 = -0.6	4.90			-1.6	2.83
$d^5$			-1.2 +1.2 = -0.0	5.92			-2.0	1.73
$d^6$			-1.6 +1.2 = -0.4	4.90			-2.4	0.00
$d^7$			-2.0 +1.2 = -0.8	3.87			-2.4 +0.6 = -1.8	1.73
$d^8$			-2.4 +1.2 = -1.2	2.83			-2.4 +1.2 = -1.2	2.83
$d^9$			-2.4 +1.8 = -0.6	1.73			-2.4 +1.8 = -0.6	1.73
$d^{10}$			-2.4 +2.4 = -0.0	0.00			-2.4 +2.4 = -0.0	0.00

## 5.10 | EFFECTS OF CRYSTAL FIELD SPLITTING

In octahedral complexes, the filling of  $t_{2g}$  orbitals decreases the energy of a complex, that is makes it more stable by  $-0.4 \Delta_o$  per electron. Filling  $e_g$  orbitals increases the energy by  $+0.6 \Delta_o$  per electron. The total crystal field stabilization energy is given by

$$\text{CFSE}_{(\text{octahedral})} = -0.4n_{(t_{2g})} + 0.6n_{(e_g)}$$

where  $n_{(t_{2g})}$  and  $n_{(e_g)}$  are the number of electrons occupying the  $t_{2g}$  and  $e_g$  orbitals respectively. The CFSE is zero for ions with  $d^0$  and  $d^{10}$  configurations in both strong and weak ligand fields. The CFSE is also zero for  $d^5$  configurations in a weak field. All the other arrangements have some CFSE, which increases the thermodynamic stability of the complexes. Thus many transition metal compounds have a higher measured lattice energy (obtained by calculations using the terms in the Born–Haber cycle) than is calculated using the Born–Landé, Born–Meyer or Kapustinskii equations. In contrast, the measured (Born–Haber) and calculated values for compounds of the main groups (which have no CFSE) are in close agreement (Table 5.12). There is also close agreement in  $\text{MnF}_2$  which has a  $d^5$  configuration and a weak field ligand; hence there is no CFSE.

**Table 5.12** Measured and calculated lattice energies

Compound	Structure	Measured lattice energy ( $\text{kJ mol}^{-1}$ )	Calculated lattice energy ( $\text{kJ mol}^{-1}$ )	Difference (measured – calculated) ( $\text{kJ mol}^{-1}$ )
NaCl	Sodium chloride	–764	–764	0
AgCl	Sodium chloride	–916	–784	–132
AgBr	Sodium chloride	–908	–759	–149
$\text{MgF}_2$	Rutile	–2908	–2915	+7
$\text{MnF}_2$	Rutile	–2770	–2746	–24
$\text{FeF}_2$	Rutile	–2912	–2752	–160
$\text{NiF}_2$	Rutile	–3046	–2917	–129
$\text{CuF}_2$	Rutile	–3042	–2885	–157

A plot of the lattice energies of the halides of the first row transition elements in the divalent state is given in Figure 5.12. In the solid, the coordination number of these metals is 6, and so the structures are analogous to octahedral complexes. The graphs for each halide show a minimum at  $\text{Mn}^{2+}$ , which has a  $d^5$  configuration. In a weak field this has a high-spin arrangement with zero CFSE. The configurations  $d^0$  and  $d^{10}$  also have zero CFSE. The broken line through  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  represents zero stabilization. The heights of other points above this line are the crystal field stabilization energies.

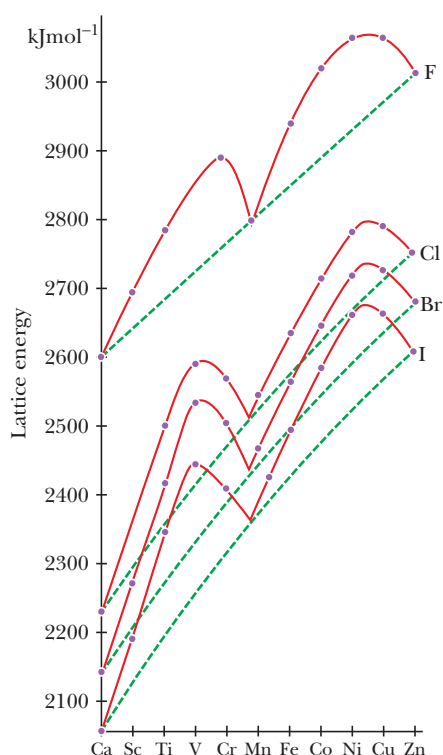
The hydration energies of the  $\text{M}^{2+}$  ions of the first row transition elements are plotted in Figure 5.13a.



The ions  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  have  $d^0$ ,  $d^5$  and  $d^{10}$  configurations, and have zero CFSE. An almost straight line can be drawn through these points. The distance of the other points above this line corresponds to the CFSE. Values obtained in this way agree with those obtained spectroscopically. A similar graph of the  $\text{M}^{3+}$  ions is shown in Figure 5.13b: here the  $d^0$ ,  $d^5$  and  $d^{10}$  species are  $\text{Sc}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ga}^{3+}$ .

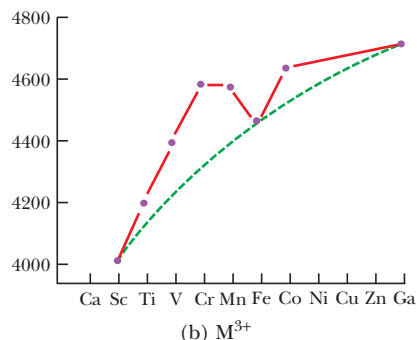
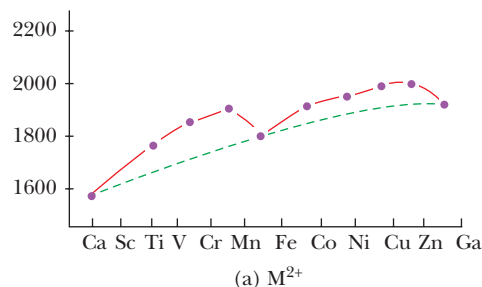
The ionic radii for  $\text{M}^{2+}$  ions might be expected to decrease smoothly from  $\text{Ca}^{2+}$  to  $\text{Zn}^{2+}$  because of the increasing nuclear charge, and the poor shielding by  $d$  electrons. A plot of these radii is given in Figure 5.14. The change in size is not regular.

A smooth (broken) line is drawn through  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$ . These have  $d^0$ ,  $d^5$  and  $d^{10}$  configurations as the  $d$  orbitals are empty, half full or full. These arrangements constitute an almost spherical field round the nucleus. In  $\text{Ti}^{2+}$  the  $d$  electrons occupy orbitals away from the ligands, providing little or no shielding of the nuclear charge. Thus the ligands are drawn closer to the nucleus. The increased nuclear charge has an even greater effect in the case of  $\text{V}^{2+}$ . At  $\text{Cr}^{2+}$  the  $e_g$  level contains one electron. This is concentrated

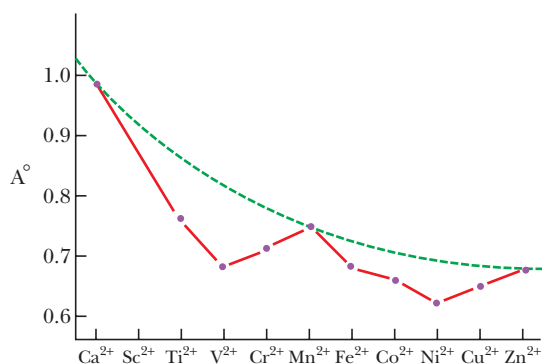


**Figure 5.12** CFSE of dihalides of the first transition series. (After T.C. Waddington. Lattice energies and their significance in inorganic chemistry. *Advances in Inorganic Chemistry and Radiochemistry*, 1, Academic Press, New York, 1959.)

in the direction of the ligands, thus providing very good shielding. Thus the ligands can no longer approach so closely and the ionic radius increases. This increase in size is continued with the filling of the second  $e_g$  orbital at  $Mn^{2+}$ . The screening by the  $e_g$  orbitals is so good that the radius of  $Mn^{2+}$  is slightly smaller than it would be if it were in a truly spherical field. The same sequence of size changes is repeated in the second half of the series.



**Figure 5.13** Enthalpies of hydration for (a)  $M^{2+}$  and (b)  $M^{3+}$ , in  $\text{kJ mol}^{-1}$ .















**Figure 5.14** Octahedral ionic radii of  $M^{2+}$  for first row transition elements.

## 5.11 | TETRAGONAL DISTORTION OF OCTAHEDRAL COMPLEXES (JAHN-TELLER DISTORTION)

The shape of transition metal complexes is determined by the tendency of electron pairs to occupy positions as far away from each other as possible. This is the same as for the main group compounds and complexes. In addition, the shapes of transition metal complexes are affected by whether the  $d$  orbitals are symmetrically or asymmetrically filled.



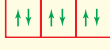



Repulsion by six ligands in an octahedral complex splits the  $d$  orbitals on the central metal into  $t_{2g}$  and  $e_g$  levels. It follows that there is a corresponding repulsion between the  $d$  electrons and the ligands. If the  $d$  electrons are symmetrically arranged, they will repel all six ligands equally. Thus the structure will be a completely regular octahedron. The symmetrical arrangements of  $d$  electrons are shown in Table 5.13.

Table 5.13 Symmetrical electronic arrangements

Electronic configuration	$t_{2g}$	$e_g$	Nature of ligand field	Examples
$d^0$			Strong or weak	$\text{Ti}^{\text{IV}}\text{O}_2$ , $[\text{Ti}^{\text{IV}}\text{F}_6]^{2-}$ $[\text{Ti}^{\text{IV}}\text{Cl}_6]^{2-}$
$d^3$			Strong or weak	$[\text{Cr}^{\text{III}}(\text{oxalate})_3]^{3-}$ $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$
$d^5$			Weak	$[\text{Mn}^{\text{II}}\text{F}_6]^{4-}$ $[\text{Fe}^{\text{III}}\text{F}_6]^{3-}$
$d^6$			Strong	$[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$
$d^8$			Weak	$[\text{Ni}^{\text{II}}\text{F}_6]^{4-}$ $[\text{Ni}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$
$d^{10}$			Strong or weak	$[\text{Zn}^{\text{II}}(\text{NH}_3)_6]^{2+}$ $[\text{Zn}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$

All other arrangements have an asymmetrical arrangement of  $d$  electrons. If the  $d$  electrons are asymmetricaly arranged, they will repel some ligands in the complex more than others. Thus the structure is distorted because some ligands are prevented from approaching the metal as closely as others. The  $e_g$  orbitals point directly at the ligands. Thus asymmetric filling of the  $e_g$  orbitals results in some ligands being repelled more than others. This causes a significant distortion of the octahedral shape. In contrast the  $t_{2g}$  orbitals do not point directly at the ligands, but point in between the ligand directions. Thus asymmetric filling of the  $t_{2g}$  orbitals has only a very small effect on the stereochemistry. Distortion caused by asymmetric filling of the  $t_{2g}$  orbitals is usually too small to measure. The electronic arrangements which will produce a large distortion are shown in Table 5.14.

Table 5.14 Asymmetrical electronic arrangements

Electronic configuration	$t_{2g}$	$e_g$	Nature of ligand field	Examples
$d^4$			Weak field (high-spin complex)	Cr (+ II), Mn (+ III)
$d^7$			Strong field (low-spin complex)	Co (+ II), Ni (+ III)
$d^9$			Either strong or weak	Cu (+ II)

The two  $e_g$  orbitals  $d_{x^2-y^2}$  and  $d_{z^2}$  are normally degenerate. However, if they are asymmetrically filled then this degeneracy is destroyed, and the two orbitals are no longer equal in energy. If the  $d_{z^2}$  orbital contains one more electron than the  $d_{x^2-y^2}$  orbital then the ligands approaching along  $+z$  and  $-z$  will encounter greater repulsion than the other four ligands. The repulsion and distortion result in elongation of the octahedron along the  $z$  axis. This is called tetragonal distortion. Strictly it should be called tetragonal elongation. This form of distortion is commonly observed.

If the  $d_{x^2-y^2}$  orbital contains the extra electron, then elongation will occur along the  $x$  and  $y$  axes. This means that the ligands approach more closely along the  $z$  axis. Thus there will be four long bonds and two short bonds. This is equivalent to compressing the octahedron along the  $z$  axis and is called tetragonal compression. Tetragonal elongation is much more common than tetragonal compression, and it is not possible to predict which will occur.

For example, the crystal structure of  $\text{CrF}_2$  is a distorted rutile ( $\text{TiO}_2$ ) structure.  $\text{Cr}^{2+}$  is octahedrally surrounded by six  $\text{F}^-$ , and there are four  $\text{Cr}-\text{F}$  bonds of length 1.98–2.01 Å, and two longer bonds of length

2.43 Å. The octahedron is said to be tetragonally distorted. The electronic arrangement in  $\text{Cr}^{2+}$  is  $d^4$ .  $\text{F}^-$  is a weak field ligand, and so the  $t_{2g}$  level contains three electrons and the  $e_g$  level contains one electron. The  $d_{x^2-y^2}$  orbital has four lobes whilst the  $d_{z^2}$  orbital has only two lobes pointing at the ligands. To minimize repulsion with the ligands, the single  $e_g$  electron will occupy the  $d_{z^2}$  orbital. This is equivalent to splitting the degeneracy of the  $e_g$  level so that  $d_{z^2}$  is of lower energy, i.e. more stable, and  $d_{x^2-y^2}$  is of higher energy, i.e. less stable. Thus the two ligands approaching along the  $+z$  and  $-z$  directions are subjected to greater repulsion than the four ligands along  $+x$ ,  $-x$ ,  $+y$  and  $-y$ . This causes tetragonal distortion with four short bonds and two long bonds. In the same way  $\text{MnF}_3$  contains  $\text{Mn}^{3+}$  with a  $d^4$  configuration, and forms a tetragonally distorted octahedral structure.

Many  $\text{Cu(II)}$  salts and complexes also show tetragonally distorted octahedral structures.  $\text{Cu}^{2+}$  has a  $d^9$  configuration:



To minimize repulsion with the ligands, two electrons occupy the  $d_{z^2}$  orbital and one electron occupies the  $d_{x^2-y^2}$  orbital. Thus the two ligands along  $-z$  and  $+z$  are repelled more strongly than are the other four ligands.

The examples above show that whenever the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals are unequally occupied, distortion occurs. This is known as Jahn–Teller distortion. The Jahn–Teller theorem states that ‘Any non-linear molecular system in a degenerate electronic state will be unstable, and will undergo some sort of distortion to lower its symmetry and remove the degeneracy.’ More simply, molecules or complexes (of any shape except linear), which have an unequally filled set of orbitals (either  $t_{2g}$  or  $e_g$ ), will be distorted. In octahedral complexes distortions from the  $t_{2g}$  level are too small to be detected. However, distortions resulting from uneven filling of the  $e_g$  orbitals are very important.

## 5.12 | SQUARE PLANAR ARRANGEMENTS

If the central metal ion in a complex has a  $d^8$  configuration, six electrons will occupy the  $t_{2g}$  orbitals and two electrons will occupy the  $e_g$  orbitals. The arrangement is the same in a complex with weak field ligands. The electrons are arranged as shown in Figure 5.15. The orbitals are symmetrically filled, and a regular octahedral complex is formed, for example by  $[\text{Ni}^{II}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Ni}^{II}(\text{NH}_3)_6]^{2+}$ .

The single electron in the  $d_{x^2-y^2}$  orbital is being repelled by four ligands, whilst the electron in the  $d_{z^2}$  orbital is only being repelled by two ligands. Thus the energy of the  $d_{x^2-y^2}$  increases relative to that of  $d_{z^2}$ . If the ligand field is sufficiently strong, the difference in energy between these two orbitals becomes larger than the energy needed to pair the electrons. Under these conditions, a more stable arrangement arises when both the  $e_g$  electrons pair up and occupy the lower energy  $d_{z^2}$  orbital. This leaves the  $d_{x^2-y^2}$  orbital empty (Figure 5.16). Thus four ligands can now approach along the  $+x$ ,  $-x$ ,  $+y$  and  $-y$  directions without any difficulty, as the  $d_{x^2-y^2}$  orbital is empty. However, ligands approaching along the  $+z$  and  $-z$  directions meet very strong repulsive forces from the filled  $d_{z^2}$  orbital (Figure 5.17). Thus only four ligands succeed in bonding to the metal. A square planar complex is formed, the attempt to form an octahedral complex being unsuccessful.

The amount of tetragonal distortion that occurs depends on the particular metal ion and ligands. Sometimes the tetragonal distortion may become so large that the  $d_{z^2}$  orbital is lower in energy than the  $d_{xy}$  orbital as shown in Figure 5.18. In square planar complexes of  $\text{Co}^{II}$ ,  $\text{Ni}^{II}$  and  $\text{Cu}^{II}$  the  $d_{z^2}$  orbital has nearly the same energy as the  $d_{xz}$  and  $d_{yz}$  orbitals. In  $[\text{PtCl}_4]^{2-}$  the  $d_{z^2}$  orbital is lower in energy than the  $d_{xz}$  and  $d_{yz}$  orbitals.

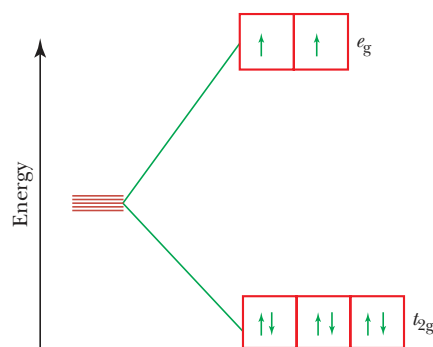
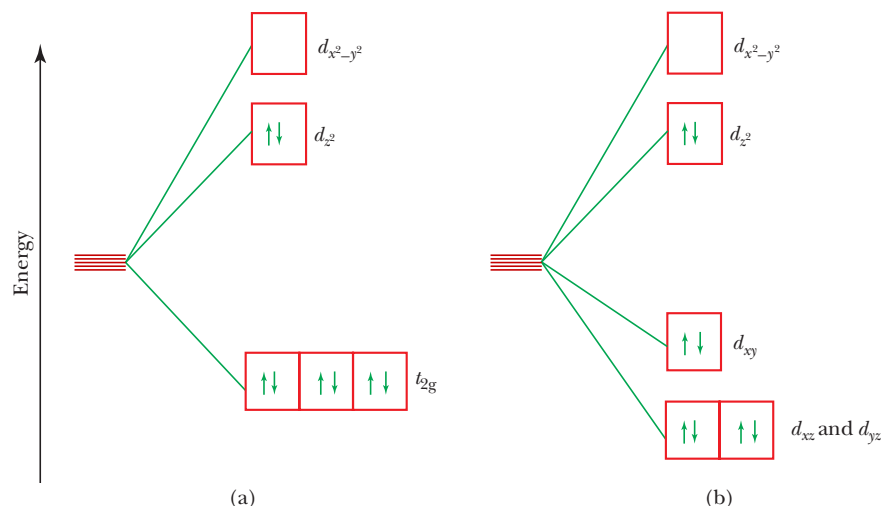
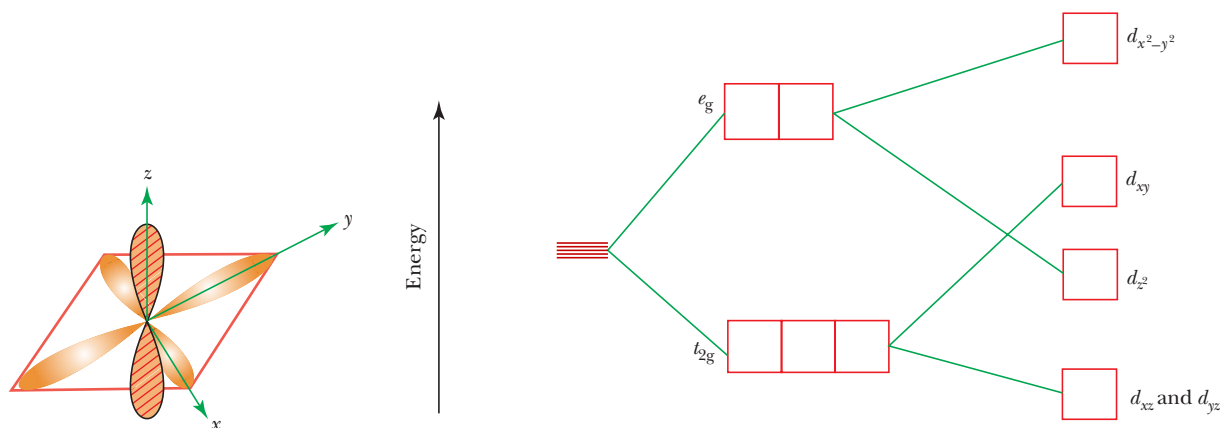


Figure 5.15  $d^8$  arrangement in weak octahedral field.



**Figure 5.16**  $d^8$  arrangement in very strong octahedral field. Tetragonal distortion splits (a) the  $e_g$  level; and (b) also splits the  $t_{2g}$  level. The  $d_{xy}$  orbital is higher in energy than the  $d_{xz}$  or  $d_{yz}$ . (For simplicity this is sometimes ignored.)



**Figure 5.17**  $d^8$  arrangement, strong field. (The  $d_{z^2}$  orbital is full, the  $d_{x^2-y^2}$  empty.)

**Figure 5.18** Tetragonal distortion.

Square planar complexes are formed by  $d^8$  ions with strong field ligands, for example  $[\text{Ni}^{\text{II}}(\text{CN})_4]^{2-}$ . The crystal field splitting  $\Delta_o$  is larger for second and third row transition elements, and for more highly charged species. All the complexes of  $\text{Pt}(\text{+II})$  and  $\text{Au}(\text{+III})$  are square planar – including those with weak field ligands such as halide ions.

Square planar structures can also arise from  $d^4$  ions in a weak ligand field. In this case the  $d_{z^2}$  orbital only contains one electron. Some ions that form square planar complexes are given in Table 5.15.

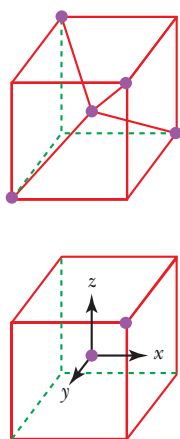
**Table 5.15** Ions that form square planar complexes

Electronic configuration	Ions	Type of field	Number of unpaired electrons
$d^4$	$\text{Cr}(\text{+II})$	Weak	4
$d^6$	$\text{Fe}(\text{+II})$	(Haem)	2
$d^7$	$\text{Co}(\text{+II})$	Strong	1
$d^8$	$\text{Ni}(\text{+II}), \text{Rh}(\text{+I}), \text{Ir}(\text{+I})$	Strong	0
	$\text{Pd}(\text{+II}), \text{Pt}(\text{+II}), \text{Au}(\text{+III})$	Strong and weak	0
$d^9$	$\text{Cu}(\text{+II}), \text{Ag}(\text{+II})$	Strong and weak	1

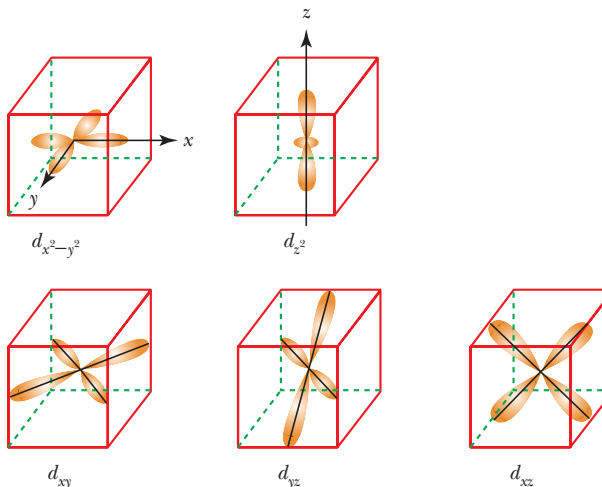
## 5.13 | TETRAHEDRAL COMPLEXES

A regular tetrahedron is related to a cube. One atom is at the centre of the cube, and four of the eight corners of the cube are occupied by ligands as shown in Figure 5.19.

The directions  $x$ ,  $y$  and  $z$  point to the centres of the faces of the cube. The  $e_g$  orbitals point along  $x$ ,  $y$  and  $z$  (that is to the centres of the faces). The  $t_{2g}$  orbitals point between  $x$ ,  $y$  and  $z$  (that is towards the centres of the edges of the cube) (Figure 5.20).



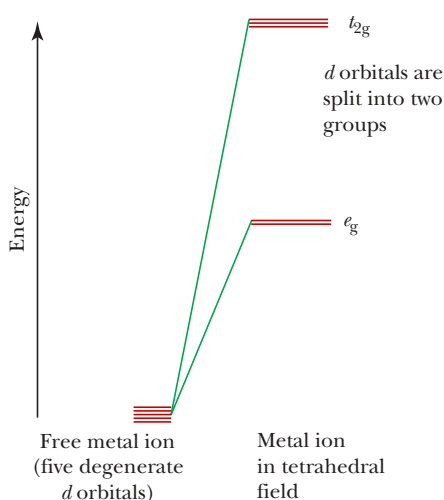
**Figure 5.19** Relation of a tetrahedron to a cube.



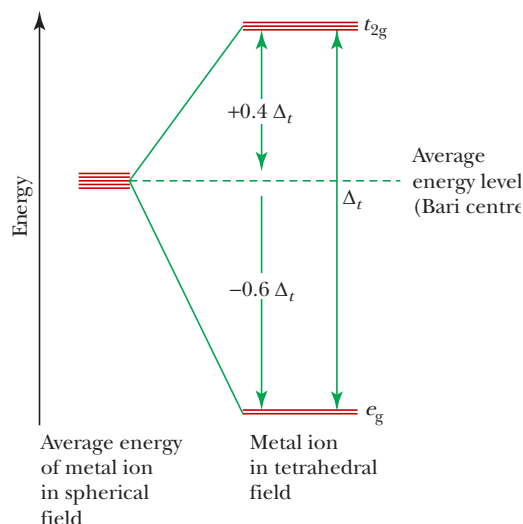
**Figure 5.20** Orientation of  $d$  orbitals relative to a cube.

The direction of approach of the ligands does not coincide exactly with either the  $e_g$  or the  $t_{2g}$  orbitals. The angle between an  $e_g$  orbital, the central metal and the ligand is half the tetrahedral angle  $= 109^\circ 28' / 2 = 54^\circ 44'$ . The angle between a  $t_{2g}$  orbital, the central metal and the ligand is  $35^\circ 16'$ . Thus the  $t_{2g}$  orbitals are nearer to the direction of the ligands than the  $e_g$  orbitals. (Alternatively the  $t_{2g}$  orbitals are half the side of the cube away from the approach of the ligands, whilst the  $e_g$  orbitals are half the diagonal of the cube away.) The approach of the ligands raises the energy of both sets of orbitals. The energy of the  $t_{2g}$  orbitals is raised most because they are closest to the ligands. This crystal field splitting is the opposite way round to that in octahedral complexes (Figure 5.21).

The  $t_{2g}$  orbitals are  $0.4\Delta_t$  above the weighted average energy of the two groups (the Bari centre) and the  $e_g$  orbitals are  $0.6\Delta_t$  below the average (Figure 5.22).



**Figure 5.21** Crystal field splitting of energy levels in a tetrahedral field.



**Figure 5.22** Energy levels for  $d$  orbitals in a tetrahedral field.



The magnitude of the crystal field splitting  $\Delta_t$  in tetrahedral complexes is considerably less than in octahedral fields. There are two reasons for this:

1. There are only four ligands instead of six, so the ligand field is only two thirds the size: hence the ligand field splitting is also two thirds the size
2. The direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly a further two thirds.

Thus the tetrahedral crystal field splitting  $\Delta_t$  roughly  $2/3 \times 2/3 = 4/9$  of the octahedral crystal field splitting  $\Delta_o$ . Strong field ligands cause a bigger energy difference between  $t_{2g}$  and  $e_g$  than weak field ligands. However, the tetrahedral splitting  $\Delta_t$  is always much smaller than the octahedral splitting  $\Delta_o$ . Thus it is never energetically favourable to pair electrons, and all tetrahedral complexes are high-spin.

**Table 5.16** CFSE and electronic arrangements in tetrahedral complexes

Number of $d$ electrons	Arrangement of electrons		Spin only magnetic moment $\mu$ (e)	Tetrahedral CFSE $\Delta_t$	Tetrahedral CFSE scaled for comparison with octahedral values, assuming $\Delta_t = \frac{4}{9}\Delta_o$	Octahedral CFSE $\Delta_o$	
	$e_g$	$t_{2g}$				Weak field	Strong field
$d^1$			1.73	-0.6	-0.27	-0.4	-0.4
$d^2$			2.83	-1.2	-0.53	-0.8	-0.8
$d^3$			3.87	$-1.2 + 0.4 = -0.8$	-0.36	-1.2	-1.1
$d^4$			4.90	$-1.2 + 0.8 = -0.4$	-0.18	-0.6	-1.6
$d^5$			5.92	$-1.2 + 1.2 = 0.0$	-0.00	0.0	-2.0
$d^6$			4.90	$-1.8 + 1.2 = -0.6$	-0.27	-0.4	-2.4
$d^7$			3.87	$-2.4 + 1.2 = -1.2$	-0.53	-0.8	-1.8
$d^8$			2.83	$-2.4 + 1.6 = -0.8$	-0.36	-1.2	-1.2
$d^9$			1.73	$-2.4 + 2.0 = -0.4$	-0.18	-0.6	-0.6
$d^{10}$			0.00	$-2.4 + 2.4 = 0.0$	0.00	0.0	0.0

The CFSE in both octahedral and tetrahedral environments is given in Table 5.16. This shows that for  $d^0$ ,  $d^5$  and  $d^{10}$  arrangements the CFSE is zero in both octahedral and tetrahedral complexes. For all other electronic arrangements there is some CFSE, and the octahedral CFSE is greater than the tetrahedral CFSE. It follows that octahedral complexes are generally more stable and more common than tetrahedral complexes. This is partly because there are six bond energy terms rather than four, and partly because there is a larger CFSE term. Despite this some tetrahedral complexes are formed, and are stable. Tetrahedral complexes are favoured:

1. Where the ligands are large and bulky and could cause crowding in an octahedral complex.
2. Where attainment of a regular shape is important. For tetrahedral structures  $d^0$ ,  $d^2$ ,  $d^5$ ,  $d^7$  and  $d^{10}$  configurations are regular. Some tetrahedral complexes which are regular are:  $\text{Ti}^{\text{IV}}\text{Cl}_4$  ( $e_g^0, t_{2g}^0$ ),  $[\text{Mn}^{\text{VII}}\text{O}_4]^-$  ( $e_g^0, t_{2g}^0$ ),  $[\text{Fe}^{\text{VI}}\text{O}_4]^{2-}$  ( $e_g^2, t_{2g}^0$ ),  $[\text{Fe}^{\text{III}}\text{Cl}_4]^-$  ( $e_g^2, t_{2g}^3$ ),  $[\text{Co}^{\text{II}}\text{Cl}_4]^{2-}$  ( $e_g^4, t_{2g}^3$ ) and  $[\text{Zn}^{\text{II}}\text{Cl}_4]^{2-}$  ( $e_g^4, t_{2g}^6$ ).
3. When the ligands are weak field, and the loss in CFSE is thus less important.
4. Where the central metal has a low oxidation state. This reduces the magnitude of  $\Delta$ .



5. Where the electronic configuration of the central metal is  $d^0$ ,  $d^5$  or  $d^{10}$  as there is no CFSE.
6. Where the loss of CFSE is small, e.g.  $d^1$  and  $d^6$  where the loss in CFSE is  $0.13\Delta_o$  or  $d^2$  and  $d^7$  where the loss is  $0.27\Delta_o$ .

Many transition metal chlorides, bromides and iodides form tetrahedral structures.

## 5.14 | MAGNETISM

The magnetic moment can be measured using a Gouy balance. If we assume that the magnetic moment arises entirely from unpaired electron spins then the 'spin only' formula can be used to estimate  $n$ , the number of unpaired electrons. This gives reasonable agreement for complexes of the first row of transition metals.

$$\mu_s = \sqrt{n(n+2)}$$

Once the number of unpaired electrons is known, either the valence bond or the crystal field theory can be used to work out the shape of the complex, the oxidation state of the metal, and, for octahedral complexes, whether inner or outer  $d$  orbitals are used. For example, Co (+III) forms many complexes, all of which are octahedral. Most of them are diamagnetic, but  $[\text{CoF}_6]^{3-}$  is paramagnetic with an observed magnetic moment of 5.3 BM. Crystal field theory explains this (Figure 5.23).

Co(+II) forms both tetrahedral and square planar four-coordinate complexes. These can be distinguished by magnetic measurements (Figure 5.24).

However, orbital angular momentum also contributes to a greater or lesser degree to the magnetic moment. For the second and third row transition elements not only is this contribution significant, but spin orbit coupling may occur. Because of this, the 'spin only' approximation is no longer valid, and there is extensive temperature-dependent paramagnetism. Thus the simple interpretation of magnetic moments in terms of the number of unpaired electrons cannot be extended from the first row of transition elements to the second and third rows. The temperature dependence is explained by the spin orbit coupling. This removes the degeneracy from the lowest energy level in the ground state. Thermal energy then allows a variety of levels to be populated.

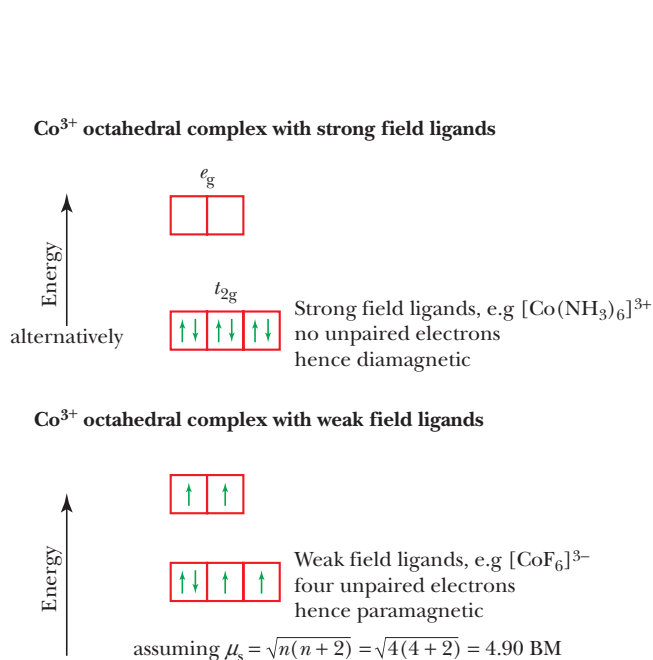


Figure 5.23 Co<sup>3+</sup> in high-spin and low-spin complexes.

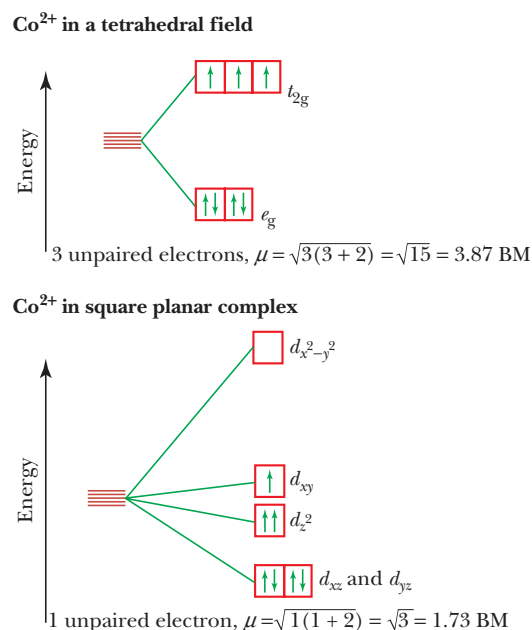


Figure 5.24 Co<sup>2+</sup> in tetrahedral and square planar complexes.

## 5.15 | EXTENSION OF THE CRYSTAL FIELD THEORY TO ALLOW FOR SOME COVALENCY

The crystal field theory is based on purely electrostatic attraction. At first sight this seems to be a most improbable assumption. Nevertheless, the theory is remarkably successful in explaining the shapes of complexes, their spectra and their magnetic properties. Calculations can be carried out quite simply. The disadvantage of the theory is that it ignores evidence that some covalent bonding does occur in at least some transition metal complexes:

1. Compounds in the zero oxidation state such as nickel carbonyl  $[\text{Ni}^0(\text{CO})_4]$  have no electrostatic attraction between the metal and the ligands. Thus the bonding must be covalent.
2. The order of ligands in the spectrochemical series cannot be explained solely on electrostatic grounds.
3. There is some evidence from nuclear magnetic resonance and electron spin resonance that there is some unpaired electron density on the ligands. This suggests the sharing of electrons, and hence some covalency.

The Racah interelectron repulsion parameter  $B$  is introduced into the interpretation of spectra. This makes allowance for covalency arising from the delocalization of  $d$  electrons from the metal onto the ligand. If  $B$  is reduced below the value for a free metal ion, the  $d$  electrons are delocalized onto the ligand. The more  $B$  is reduced the greater the delocalization and the greater the amount of covalency. In a similar way an electron delocalization factor  $k$  can be used in interpreting magnetic measurements.

## 5.16 | NOMENCLATURE OF COORDINATION COMPOUNDS

The rules for systematic naming of coordination compounds are discussed as follows:

1. The name of the cationic part is written first followed by the anionic part.
2. The name of the ligand is listed before the name(s) of the central atom(s).
3. No space is left between the names that refer to the same coordination entity.
4. Ligand names are listed in the alphabetical order (multiplicative prefixes indicating the number of ligands are not considered in determining that order).
5.
  - a. When there are several ligands of the same kind, prefixes like di, tri, tetra, penta, hexa, etc. are used before the name of the ligand to indicate their number.
  - b. When the name of the ligand includes terms like di, tri, tetra, etc. then prefixes like bis, tris, tetrakis, pentakis, etc. are written before the name of the ligand, and the ligand name is kept within brackets to avoid ambiguity. For example,
    - (i)  $(\text{NH}_3)_2$ : diammine
    - (ii)  $\text{Me}_2\text{NH}$ : dimethylamine
    - (iii)  $(\text{en})_2$ : bis (ethylenediamine)
    - (iv)  $(\text{NH}_2\text{Me})_2$ : bis (methylamine)  
(to make it distinct from dimethylamine)
  - c. There is no deletion of vowels or use of a hyphen. For example,  $(\text{NH}_3)_4$ : tetraammine.
6. The names of cationic ligands are ended with 'ium'. For example,
  - (i)  $\text{NO}^+$ : nitrosylium
  - (ii)  $\text{NH}_2 - \text{NH}_3^+$ : hydrazinium
7. The neutral ligand names have no special endings. For example,
  - (i)  $\text{H}_2\text{O}$ : aqua
  - (ii)  $\text{NH}_3$ : ammine
  - (iii)  $\text{CO}$ : carbonyl
  - (iii)  $\text{NO}$ : nitrosyl

- (iv)  $\text{MeCONH}_2$ : acetamide
- (v)  $\text{MeNH}_2$ : methanamine
- (vi)  $\text{MePH}_2$ : methylphosphane
- (vii)  $\text{Me O S(=O)OH}$ : methyl hydrogen sulphite
- (ix)  $\text{Me}_2\text{O}$ : dimethyl ether
- (x)  $\text{Me}_2\text{S}$ : dimethyl thioether
- (xi)  $\text{C}_6\text{H}_6$ : benzene

8. The names of anionic ligands are ended with 'o'. For example,

a. Ligand names ending with 'ate' are changed to 'ato'.

- (i)  $\text{NO}_3^-$ : nitrato
- (ii)  $\text{CO}_3^{2-}$ : carbonato
- (iii)  $\text{MeCO}_2^-$ : acetato or ethanoato
- (iv)  $\text{acac}^-$ : acetylacetonato

b. Ligand names ending with 'ite' are changed to 'ito'.

- (i)  $\text{SO}_3^{2-}$ : sulphito
- (ii)  $\text{ClO}_2^-$ : chlorito
- (iii)  $\text{OCl}^-$ : hypochlorito
- (iv)  $\text{NO}_2^-$ : nitrito

c. Ligand names ending with 'ide' are changed to 'ido'.

- (i)  $\text{F}^-$ : fluorido
- (ii)  $\text{Cl}^-$ : chlorido
- (iii)  $\text{CN}^-$ : cyanido
- (iv)  $\text{H}^-$ : hydrido
- (v)  $\text{OH}^-$ : hydroxido
- (vi)  $\text{NH}_2^-$ : amido
- (vii)  $\text{D}^-$ : deuterido or  $[^2\text{H}]$  hydrido

d. The anionic organic ligands where the C atom is the donor atom, are not ended with 'o'. For example,

- (i)  $\text{CH}_3^-$ : methyl (not methylo)
- (ii)  $\text{CH}_2\text{CH}=\text{CH}_2^-$ : allyl
- (iii)  $\text{Ph}^-$ : phenyl
- (iv)  $\text{Cyclopropyl}^-$ : cyclopropyl
- (v)  $\text{CH}_2=\text{CH}^-$ : vinyl

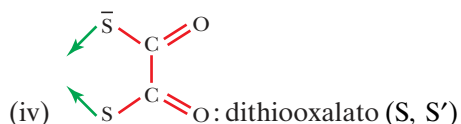
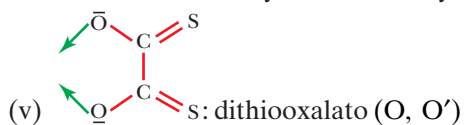
e. For the  $\pi$ -donors, the prefix like  $\eta^x$  is to be used, where  $\eta$  indicates  $\pi$ -electron donation and  $x$  is known as the hapticity of the ligand, i.e. the number of atoms involved in the  $\pi$ -donation. For example,

- (i)  $\pi\text{-C}_5\text{H}_5^-$ :  $\eta^5$  – cyclopentadienyl or pentahaptocyclopentadienyl
- (ii)  $\pi\text{-C}_6\text{H}_6^-$ :  $\eta^6$  – benzene or hexahaptobenzene
- (iii)  $\pi\text{-C}_3\text{H}_5^-$ :  $\eta^3$  – allyl or trihaptoallyl

f. Ambidentate ligands are named as follows:

- (i)  $\leftarrow\text{C}\equiv\text{N}$ : cyanido or cyanido – C  
 $\leftarrow\text{N}\equiv\text{C}$ : isocyanido or cyanido – N
- (ii)  $\leftarrow\text{NO}_2^-$ : nitro or nitrito – N  
 $\leftarrow\text{ON}\text{O}^-$ : nitrito or nitrito – O
- (iii)  $\leftarrow\text{O}\equiv\text{CN}$ : cyanato or cyanato – O  
 $\leftarrow\text{NC}\text{O}$ : isocyanato or cyanato – N

- (iv)  $\leftarrow: \bar{\text{S}}\text{CN}:$  thiocyanato or thiocyanato – S  
 $\leftarrow: \text{NC}\bar{\text{S}}:$  isothiocyanato or thiocyanato – N



9. For anionic complexes, metal names are ended with 'ate', i.e. 'ate' is to replace 'ium', 'um', or 'enum' in the metal's name. For example,

- (i) Aluminium : Aluminate  
 (ii) Platinum : Platinate  
 (iii) Molybdenum : Molybdate  
 (iv) Zinc : Zincate  
 (v) Nickel : Nickelate  
 (vi) Cobalt : Cobaltate  
 (vii) Iron : Ferrate  
 (viii) Manganese : Manganate

10. The oxidation number of the central atom is written in Roman numerals within brackets, after the name of the central atom. For example, as. (II), (–I), (0), etc.

Alternatively, the charge on a coordination entity may be indicated. The net charge is written in Arabic numerals, with the number preceding the charge sign and enclosed in parenthesis. It follows the name of the central atom (including the ending 'ate' if applicable) without the intervention of a space. For example,

- (i)  $\text{K}_4[\text{Fe}(\text{CN})_6]$ : potassium hexacyanidoferrate (II)  
 or potassium hexacyanidoferrate (4–)  
 or tetrapotassium hexacyanidoferrate  
 (ii)  $\text{K}_2[\text{OsCl}_5\text{N}]$ : potassium pentachloridonitridoosmate (2–)  
 or potassium pentachloridonitridoosmate (VI)  
 (iii)  $[\text{CuCl}_2\{\text{O}=\text{C}(\text{NH}_2)_2\}_2]^0$ : dichloridobis (urea) copper (II)  
 (iv)  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ : pentamminechloridocobalt (III) chloride  
 or pentaamminechloridocobalt (2+) chloride

11. If there is any water of crystallization, it is to included in the name. For example,

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ : tetraaquadichlorido chromium (III) chloride - 2 - water or tetraaquadichlorido chromium (III) chloride dihydrate

These rules are illustrated by the following examples:

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	Hexaamminecobalt(III) chloride
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	Pentaamminechloridocobalt(III) ion
$[\text{CoSO}_4(\text{NH}_3)_4]\text{NO}_3$	Tetraamminesulphatocobalt(III) nitrate
$[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$	Triamminetrinitrocobalt(III)
$[\text{CoCl} \cdot \text{CN} \cdot \text{NO}_2 \cdot (\text{NH}_3)_3]$	Triamminechloridocyanonitrocobalt(III)
$[\text{Zn}(\text{NCS})_4]^{2-}$	Tetrathiocyanato-N-zincate(II) ion

$[\text{Cd}(\text{SCN})_4]^{2-}$	Tetrathiocyanato-S-cadmiate(II) ion
$\text{Li}[\text{AlH}_4]$	Lithium tetrahydridoaluminate(III) ( <i>lithium aluminium hydride</i> )
$\text{Na}_2[\text{ZnCl}_4]$	Sodium tetrachloridozincate(II)
$\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O}_2)\text{NH}_3]$	Potassium amminedicyanodioxoperoxo chromate(VI)
$[\text{Pt}(\text{py})_4][\text{PtCl}_4]$	Tetrapyridineplatinum(II) tetrachloridoplatinate(II)
$[\text{Cr}(\text{en})_3]\text{Cl}_3$	<i>d</i> or <i>l</i> Tris(ethylenediamine)chromium(III) chloride
$[\text{CuCl}_2(\text{CH}_3\text{NH}_2)_2]$	Dichloridobis(methylamine)copper(II)

## 5.17 | ISOMERISM

Compounds that have the same chemical formula but different structural arrangements are called isomers. Because of the complicated formulae of many coordination compounds, the variety of bond types and the number of shapes possible, many different types of isomerism occur. Werner's classification into polymerization, ionization, hydrate linkage, coordination, coordination position, and geometric and optical isomerism is still generally accepted.

### Polymerization isomerism

This is not true isomerism because it occurs between compounds having the same empirical formula, but different molecular weights. Thus  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ ,  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ ,  $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{NH}_3)\text{Cl}_3]_2$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2[\text{PtCl}_4]$

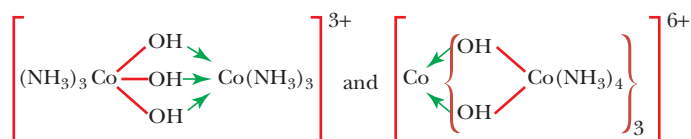


Figure 5.25 Polymerization isomers.

all have the same empirical formula. Polymerization isomerism may be due to a different number of nuclei in the complex, as shown in Figure 5.25.

### Ionization isomerism

This type of isomerism is due to the exchange of groups between the complex ion and the ions outside it.  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  is red-violet. An aqueous solution gives a white precipitate of  $\text{BaSO}_4$  with  $\text{BaCl}_2$  solution, thus confirming the presence of free  $\text{SO}_4^{2-}$  ions. In contrast  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  is red. A solution of this complex does not give a positive sulphate test with  $\text{BaCl}_2$ . It does give a cream-coloured precipitate of  $\text{AgBr}$  with  $\text{AgNO}_3$ , thus confirming the presence of free  $\text{Br}^-$  ions. Note that the sulphate ion occupies only one coordination position even though it has two negative charges. Other examples of ionization isomerism are  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$  and  $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$ , and  $[\text{Co}(\text{en})_2\text{NO}_2 \cdot \text{Cl}]\text{SCN}$ ,  $[\text{Co}(\text{en})_2\text{NO}_2 \cdot \text{SCN}]\text{Cl}$  and  $[\text{Co}(\text{en})_2\text{Cl} \cdot \text{SCN}]\text{NO}_2$ .

### Hydrate isomerism

This type of isomerism is shown by compounds having the same formula but differing only in the number of water molecules of crystallization. More broadly, it can also be called solvent isomerism to include other solvents also (like  $\text{NH}_3$  or other ligands) present in a similar manner. Some examples of hydrate isomerism are as follows

1.  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  can exist in following forms:  
 $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ ; violet (three chloride ions)

$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ : bright blue green (two chloride ions)

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ : dark green (one chloride ion)

$[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$ : dark green (no chloride ion)

2.  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Br}_2$  and  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl} \cdot \text{H}_2\text{O}$ .

3.  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3$  and  $[\text{Co}(\text{NH}_3)_5\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ .

Note that hydrate isomerism is also a kind of ionization isomerism.

## Linkage isomerism

Certain ligands contain more than one atom which could donate an electron pair. Thus this type of isomerism is shown by ambidentate ligands. For example, in the  $\text{NO}_2^-$  ion, either N or O atoms can act as the electron pair donor. Thus there is the possibility of isomerism. Two different complexes  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  have been prepared, each containing the  $\text{NO}_2^-$  group in the complex ion. One is red and is easily decomposed by acids to give nitrous acid. It contains  $\text{Co}-\text{ONO}$  and is a nitrito complex. The other complex is yellow and is stable to acids. It contains the  $\text{Co}-\text{NO}_2$  group and is a nitro compound. The two materials are represented in Figure 5.26.

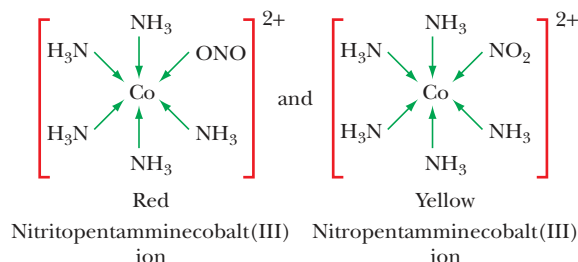
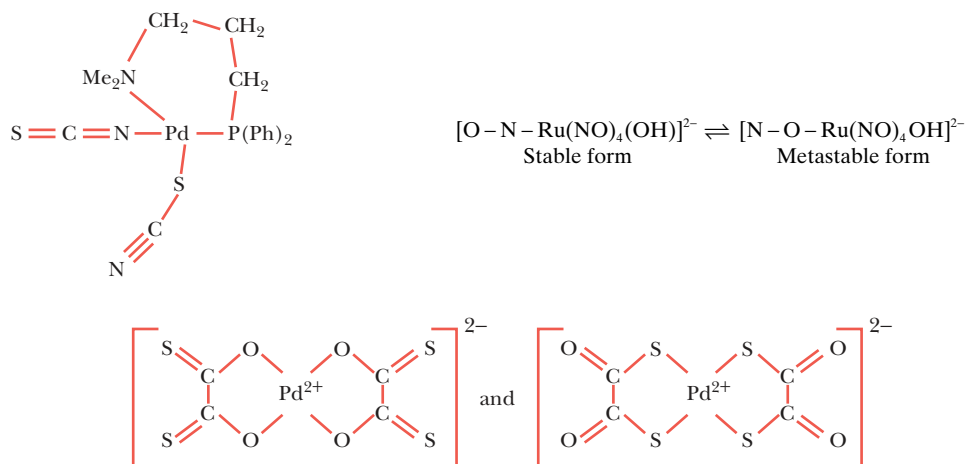


Figure 5.26 Nitrito and nitro complexes.

This type of isomerism also occurs with other ligands such as  $\text{SCN}^-$ ,  $\text{OCN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CN}^-$ ,  $\text{NOS}^-$ ,  $\text{NO}$  and  $\text{C}_2\text{O}_2\text{S}_2^{2-}$  (dithiooxalate ion). For example,



## Coordination isomerism

When both the positive and negative ions are complex ions, isomerism may be caused by the interchange of ligands between the anion and cation, for example  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ . Intermediate types between these extremes are also possible. For example,

Formula	Possible number of isomers
$[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Cr}(\text{NO}_2)_6]^{3-}$	6
$[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Co}(\text{NO}_2)_6]^{3-}$	3
$[\text{Pt}(\text{NH}_3)_4]^{2+}[\text{PtCl}_4]^{2-}$	2
$[\text{Pt}(\text{NH}_3)_4]^{2+}[\text{CuCl}_4]^{2-}$	4
$[\text{Ni}(\text{NH}_3)_6]^{3+}[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$	4
$[\text{Ni}(\text{en})_3]^{3+}[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$	4

### Coordination position isomerism

In polynuclear complexes an interchange of ligands between the different metal nuclei gives rise to positional isomerism. An example of this type of isomerism is given in Figure 5.27.

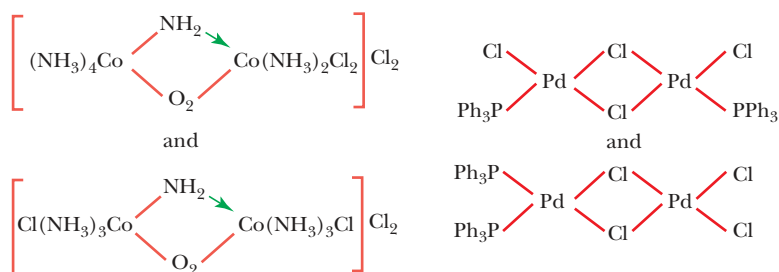


Figure 5.27 Coordination position isomers.

### Geometrical isomerism and optical isomerism

In disubstituted complexes, the substituted groups may be adjacent or opposite to each other. This gives rise to geometric isomerism. This type of isomerism is observed in complexes with coordination number four, five and six.

If a molecule is asymmetric, it cannot be superimposed on its mirror image. The molecule and its mirror image have the type of symmetry as shown by the left and right hands and are called an enantiomorph pair. The two forms are optical isomers. They are called either *dextro* or *laevo* (often shortened to *d* or *l*), depending on the direction in which they rotate the plane of polarized light in a polarimeter. (*d* rotates to the right, *l* to the left.) Optical isomerism is common in octahedral complexes involving bidentate groups.

The geometrical and optical isomerism for complexes having coordination numbers four, five and six is discussed as follows.

#### 1. For coordination number 6

The complexes with coordination number 6 can exist in octahedral geometry. The following cases may arise in complexes with octahedral geometry.

- a. All ligands are monodentate, having no chiral centre:** The various structures possible are listed below. Here M is the metal ion and a, b, c, d, e and f represent monodentate ligands.

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
$\text{Ma}_6$	1	0	1
$\text{Ma}_5\text{b}$	1	0	1

(Continued)

(Continued)

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
$\text{Ma}_4\text{b}_2$	2	0	2
$\text{Ma}_4\text{bc}$	2	0	2
$\text{Ma}_3\text{b}_3$	2	0	2
$\text{Ma}_3\text{b}_2\text{c}$	3	0	3
$\text{Ma}_3\text{bcd}$	5	1	4
$\text{Ma}_2\text{b}_2\text{c}_2$	6	1	5
$\text{Ma}_2\text{b}_2\text{cd}$	8	2	6
$\text{Ma}_2\text{bcde}$	15	6	9
$\text{Mabcdef}$	30	15	15

- b. When ligands are bidentate symmetrical and monodentate type, having no chiral centre:** The various structures possible are listed below. Here M is the metal ion, AA is a bidentate symmetrical ligand and a, b, c, and d represent monodentate ligands.

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
$[\text{M}(\text{AA})_3]$	2	1	1
$[\text{M}(\text{AA})_2\text{a}_2]$	3	1	2
$[\text{M}(\text{AA})_2\text{ab}]$	3	1	2
$[\text{M}(\text{AA})\text{a}_4]$	1	0	1
$[\text{M}(\text{AA})\text{a}_3\text{b}]$	2	0	2
$[\text{M}(\text{AA})\text{a}_2\text{b}_2]$	4	1	3
$[\text{M}(\text{AA})\text{a}_2\text{bc}]$	6	2	4
$[\text{M}(\text{AA})\text{abcd}]$	12	6	6

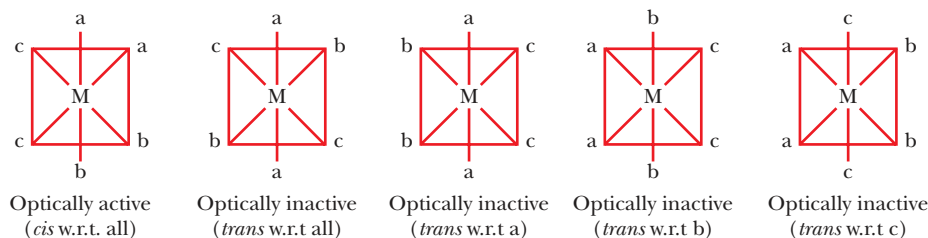
- c. When ligands are bidentate unsymmetrical and monodentate type having no chiral centre:** The various structures possible are listed below. Here M is the metal ion, AB is a bidentate unsymmetrical ligand and a, b, c, and d represent monodentate ligands.

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
$[\text{M}(\text{AB})_3]$	4	2	2
$[\text{M}(\text{AB})_2\text{a}_2]$	8	3	5
$[\text{M}(\text{AB})_2\text{ab}]$	11	5	6
$[\text{M}(\text{AB})\text{a}_4]$	1	0	1
$[\text{M}(\text{AB})\text{a}_3\text{b}]$	4	1	3
$[\text{M}(\text{AB})\text{a}_2\text{b}_2]$	6	2	4
$[\text{M}(\text{AB})\text{a}_2\text{bc}]$	12	5	7
$[\text{M}(\text{AB})\text{abcd}]$	24	12	12



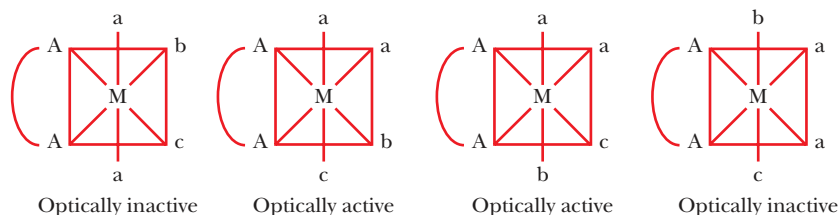
Some examples of each kind are illustrated as follows:

(i) For  $[\text{Ma}_2\text{b}_2\text{c}_2]^{n\pm}$ : The various structures possible are shown in Figure 5.28.



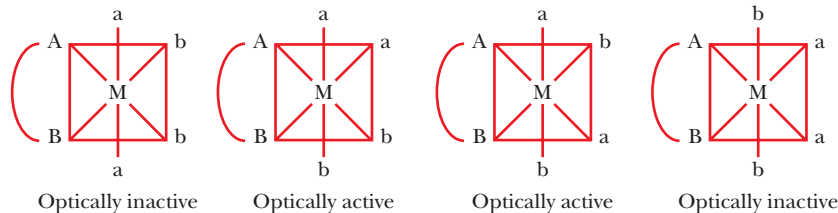
**Figure 5.28** Possible structures for octahedral complexes of the type  $[\text{Ma}_2\text{b}_2\text{c}_2]^{n\pm}$ .

(ii) For  $[\text{M}(\text{AA})_2\text{b}_2\text{c}]^{n\pm}$ : The various structures possible are shown in Figure 5.29.



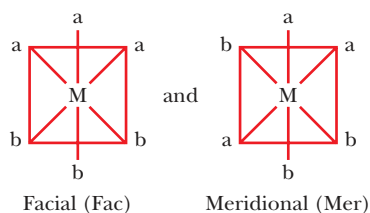
**Figure 5.29** Possible structures for octahedral complexes of the type  $[\text{M}(\text{AA})_2\text{b}_2\text{c}]^{n\pm}$ .

(iii) For  $[\text{M}(\text{AB})_2\text{a}_2\text{b}_2]^{n\pm}$ : The various structures possible are shown in Figure 5.30.



**Figure 5.30** Possible structures for octahedral complexes of the type  $[\text{M}(\text{AB})_2\text{a}_2\text{b}_2]^{n\pm}$ .

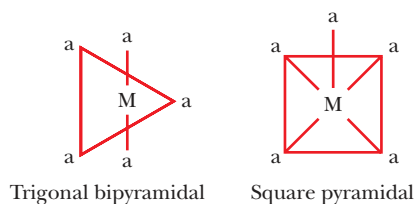
(iv) For  $\text{Ma}_3\text{b}_3$ : The various structures possible are shown in Figure 5.31.



**Figure 5.31** Possible structures for octahedral complexes of the type  $\text{Ma}_3\text{b}_3$ .

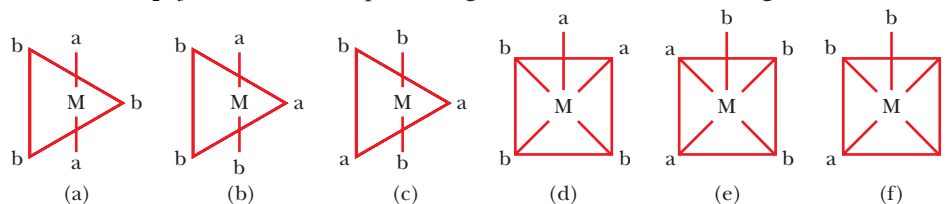
## 2. For coordination number 5

- a.** The formula  $\text{Ma}_5$  can exist in two possible geometries, i.e. trigonal bipyramidal and square pyramidal. These two are also called allomer isomers (Figure 5.32).



**Figure 5.32** Possible structures for complexes of the type  $\text{Ma}_5$ .

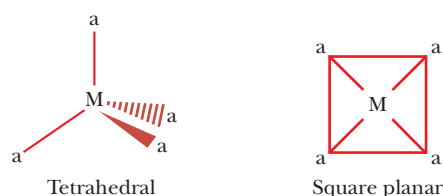
b. The formula  $\text{Ma}_2\text{b}_3$  can exist in six possible geometries as shown in Figure 5.33.



**Figure 5.33** Possible structures for complexes of the type  $\text{Ma}_2\text{b}_3$ . Here (a), (b), (c) are geometrical isomers of each other but any one of (a), (b), (c) and any one of (d), (e), (f) are allong isomers of each other.

### 3. For coordination number 4

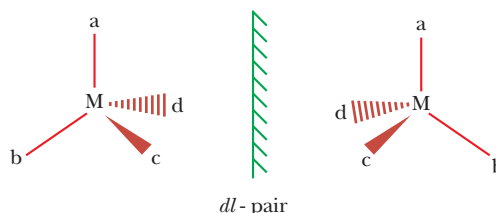
The complexes with coordination number four (e.g.  $\text{Ma}_4$ ) can have two possible geometries, i.e. tetrahedral or square planar (Figure 5.34).



**Figure 5.34** Possible structures for complexes with coordination number four.

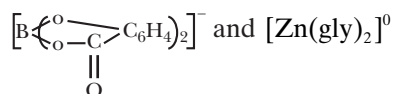
#### a. For tetrahedral geometry:

- (i) If the ligands are different, then no geometrical isomerism is observed in tetrahedral geometry, i.e. complexes of the type  $\text{Mabcd}$  exist as two optical isomers only (Figure 5.35).



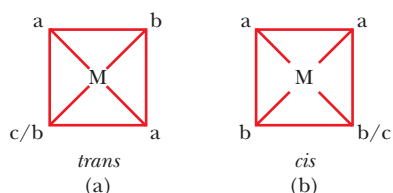
**Figure 5.35** Possible structures for complexes of the type  $\text{Mabcd}$ .

- (ii) If symmetrical bidentate ligands having no chiral center are present, then the complexes are optically inactive. For example, the following compounds are optically inactive:  $[\text{Zn}(\text{acac})_2]^0$ ,  $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$  and  $[\text{B}(\text{C}_6\text{H}_4)_2]^-$
- (iii) If unsymmetrical bidentate ligands are present, then the compound will be optically active. For example, the following compounds are optically active:



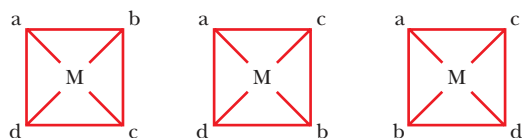
#### b. For square planar geometry:

- (i) The complexes with formula  $[\text{Ma}_4]^{n\pm}$ ,  $[\text{Ma}_3\text{b}]^{n\pm}$ ,  $[\text{M}(\text{AA})_2]^{n\pm}$ ,  $[\text{M}(\text{AA})_2\text{a}_2]^{n\pm}$  and  $[\text{M}(\text{AB})_2]^{n\pm}$  do not show geometrical isomerism since possible geometry is only one. Here, a, b are simple monodentate ligands; AA is a symmetrical bidentate ligand and AB is an unsymmetrical bidentate ligand, all having no chiral centre.
- (ii) The complexes with formulae  $[\text{Ma}_2\text{b}_2]^{n\pm}$  and  $[\text{Ma}_2\text{bc}]$  can have two geometrical isomers, as shown in Figure 5.36 a and 5.36 b respectively.



**Figure 5.36** Geometrical isomers for complexes of the type  $[Ma_2b_2]^{n\pm}$  and  $[Ma_2bc]$ .

- (iii) The complexes with formula  $[Mabcd]^{n\pm}$  can have three geometrical isomers (Figure 5.37). For these isomers, *cis* and *trans* terminology is not applicable or it is to be mentioned with respect to a, b or b, c, etc.



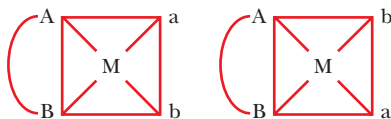
**Figure 5.37** Geometrical isomers for complexes of the type  $[Mabcd]^{n\pm}$ .

- (iv) For complex with the type  $[M(AB)_2]^{n\pm}$ , two geometrical isomers are possible (Figure 5.38).



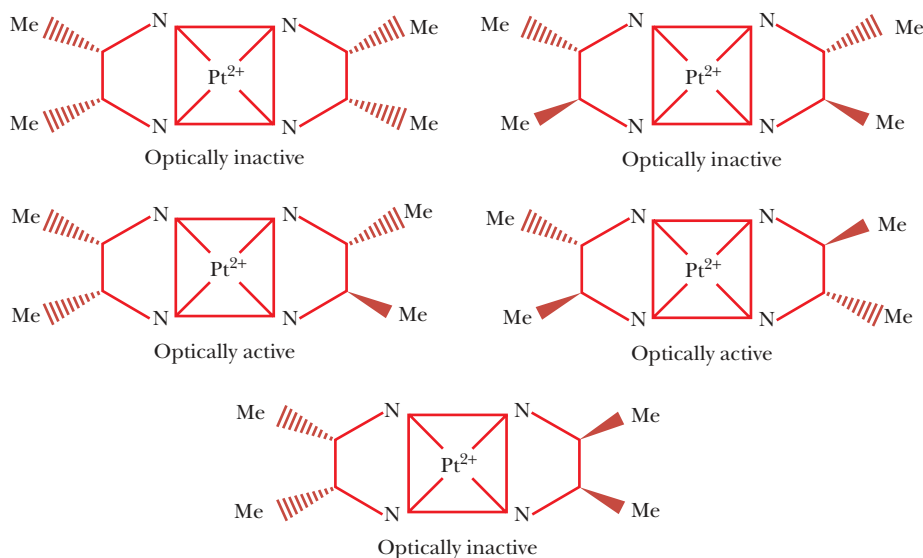
**Figure 5.38** Geometrical isomers for complexes of the type  $[M(AB)_2]^{n\pm}$ .

- (v) In complexes of the type  $[M(AB)ab]^{n\pm}$ , two geometrical isomers are possible (Figure 5.39).



**Figure 5.39** Geometrical isomers for complexes of the type  $[M(AB)ab]^{n\pm}$ .

- (vi) The complexes of the type  $[M(AA)_2]^{n\pm}$  can show geometrical isomerism if the ligand AA has a chiral centre. For example, consider the geometrical isomers of  $[Pt(bn)_2]^{2+}$  (Figure 5.40), where  $bn : CH_3 - \overset{*}{CH}(NH_2) - \overset{*}{CH}(NH_2) - CH_3$ .



**Figure 5.40** Geometrical isomers of  $[Pt(bn)_2]^{2+}$ .